PHYSICO-CHEMICAL STUDIES IN IONIC MICELLAR SYSTEMS

THESIS

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BY

DAMYANTI SHARMA

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To my dear mummy & papa

Prof. KABIR-UD-DIN
Department of Chemistry
Aligarh Muslim University
Aligarh - 202 002, INDIA

Off: 0571-703 515
Lab. 0571-700 922 (Ext. 323)
Fax : 091- 571- 708336
E-mail : kabir7@rediffmail.com

Dated: Sept. 10, 2002

CERTIFICATE

This is to certify that the thesis entitled **"Physico-chemical Studies in Ionic Micellar Systems"** is the original work carried out by **Miss Damyanti Sharma** under my supervision and is suitable for submission for the award of **Ph.D.** degree in **Chemistry**.

(Prof. Kabir-ud-Din)

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Damyanti Sharma

Damyanti Sharma

List of Publications

1. Cloud Point Phenomenon in Anionic Surfactant + Quaternary Bromide Systems and Its Variation with Additives.
   Sanjeev Kumar, Damyanti Sharma, and Kabir-ud-Din, *Langmuir*, **16**, 6821-6824 (2000).

2. Occurrence of Cloud Points in Sodium Dodecyl Sulfate–Tetra-*n*-butylammonium Bromide System.
   Sanjeev Kumar, Damyanti Sharma, Ziya Ahmad Khan, and Kabir-ud-Din, *Langmuir*, **17**, 5813-5816 (2001).

3. Role of Functional Group Position in Producing Viscoelasticity in Micellar Solutions : A ^{1}H NMR Study.
   Kabir-ud-Din, Sanjeev Kumar and Damyanti Sharma. *J. Surf. Deterg.*, **5**, 131-134 (2002).

4. Salt–Induced Cloud Point in Anionic Surfactant Solutions : Role of the Headgroup and Additives.
   Sanjeev Kumar, Damyanti Sharma, Ziya Ahmad Khan, and Kabir-ud-Din, *Langmuir*, **18**, 4205-4209 (2002).

5. Temperature – [salt] Compensation for Clouding in Ionic Micellar Systems Containing Anionic Sodium Dodecyl Sulfate and Symmetrical Quaternary Bromides.
   Sanjeev Kumar, Damyanti Sharma, and Kabir-ud-Din, *Langmuir* (communicated, Re : LA 020465Y (139)).

Papers Presented at Conferences

1. Appearance of Cloud Point in Ionic Surfactants.
   Kabir-ud-Din, Sanjeev Kumar and Damyanti Sharma
   9th National Conference on Surfactants, Emulsions and Biocolloids, Kalyani, November 2-4, (1999).

2. Cloud Point Tuning Through Additives in Sodium Dodecyl Sulphate Tetrabutylammonium Bromide System.
   Sanjeev Kumar, Damyanti Sharma, Andleeb Z. Naqvi and Kabir-ud-Din
   18th Conference of Indian Council of Chemists, Jalgaon, December 27-29 (1999).

3. Clouding by Tetra-*n*-Butylammonium Bromide in Sodium Dodecyl-benzenesulfonate Solutions.
   S. Kumar, D. Sharma and Kabir-ud-Din
   10th National Conference on Surfactants, Emulsions and Biocolloids, Shillong, October 3-5, 2001.

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Chapter - I

General Introduction

SURFace ACTive AgeNTS or surfactants owe their name to their interesting behavior at surfaces and interfaces. They are vital components in biological systems,[1,2] form key ingredients in consumer products and play important role in many industrial processes.

Man made surfactants are used in almost every branch of chemical industry as well as in several other industries. The applications range from agricultural sprays to oil recovery including areas such as catalysis, dispersions, detergency, cleaning, wetting, emulsification, foaming, and retardation of evaporation from lakes and reservoirs. Recently, surfactant based cloud point extraction methodologies (CPEM) have been successfully used to design efficient extraction techniques for the separation, preconcentration, or purification of a variety of substances including metal ions and various organic compounds.[3-10] The characteristic properties of surfactants in solution which render their possible applications depend in all cases on the tendency of these compounds to adsorb at interfaces between the solution and the adjacent gaseous, liquid, or solid phases.

When surfactants are dissolved in water, many types of aggregates can be formed. Common aggregates are micelles, either spherical, disc-like, or rod-like, vesicles, or lamellar phases. Their aggregation has been shown to be useful for the conversion of solar energy into chemical fuel, as model membranes, and in controlled drug delivery. However, in spite of a wealth of experience in the field, utilization of surfactants for a particular purpose remains more of an art than a science.

Surfactants and their Classification

Many types of substances act as surfactants, but all share the property of amphipathy: the molecule is composed of a nonpolar

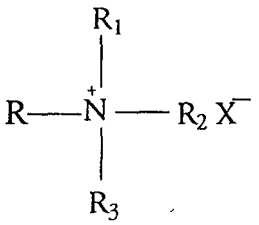
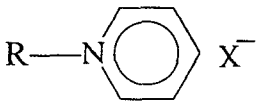
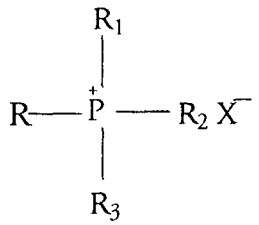
hydrophobic portion and a polar hydrophilic portion and is, therefore, partly hydrophilic and partly hydrophobic. Surfactants may be referred to as either amphiphilic or amphipathic; the terms are synonymous. The polar, hydrophilic part of the molecule is simply called the head and may be positive, negative, neutral, or zwitterionic. The nonpolar, hydrophobic part is called the tail and consists of one or more hydrocarbon chains, usually with 6-22 carbon atoms. Chains may be linear, or branched, and can be partly or completely halogenated as in fluorocarbon surfactants. The presence of a hydrophilic group makes surfactants soluble in aqueous media, and is responsible for the physico-chemical properties of aqueous surfactant solutions. The basic building blocks of surfactants are derived from petrochemicals and oleochemicals (vegetable and animal) feedstocks.

Schemes for classifying surfactants are typically based on physical properties or functionality. The most prevalent physical property used in classification is ionicity: is the surfactant charged or uncharged, ionic or nonionic? Surfactant is characterized as ionic if on dissolution in water the surface-active portion containing the hydrophobic chain has net charge. The ionic surfactants are further classified as cationic and anionic depending on whether the headgroup is positively or negatively charged.

(i) Cationic Surfactants

The most prevalent cationic surfactants are based on quaternary nitrogen. Alkylammonium halides and tetraalkylammonium halides are the most numerous in this class. Pyridine and related species such as quinoline, isoquinoline, pyrazine, and their derivatives form the basis for a wide class of aryl-based quaternary surfactants. Although less numerous, phosphorus can also be quaternized with alkyl groups to provide alkyl

phosphonium surfactants. The chemical structure of common hydrophilic groups for cationic surfactants are given below.

Chemical structure	**Name**
	Ammonium
	Pyridinium
	Phosphonium

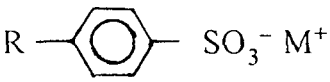
R–: long hydrophobic tail; R_1–, R_2–, R_3–: hydrogen or short alkyl chain.

(ii) Anionic Surfactants

Alkali alkanoates are the most well known anionic surfactants. The ionized carboxyl group provides the anionic charge. Alkyl sulfates, alkyl sulfonates, aryl sulfonates, such as alkylbenzene sulfonates, methylester solfonates, and sulfonates of alkylsuccinates are other important classes of anionic surfactants. The fatty acids and these sulfo compounds include the three most important anionic groups, carboxylate ($-CO_2^-$), sulfate ($-OSO_3^-$), sulfonate ($-SO_3^-$). Basicity and phase data have led to the following rank ordering of these groups with respect to their relative hydrophilicity:

$-CO_2^- >> -SO_3^- > -OSO_3^-$

Phosphate mono- ($-P(OH)O_2^-$) and dianions ($-PO_3^{--}$) are also important hydrophilic groups. While the phosphate dianions are relatively basic and protonate in the neutral to slightly alkaline range, they remain charged to relatively low pH. The much smaller carboxylate attains a higher charge density and is most hydrophobic in the series. The chemical structure of some of the hydrophilic groups for anionic surfactants are

Chemical structure	**Name**
$R-(COO^-)_n\ M^{n+}$	Carboxylate
$R-OSO_3^-\ M^+$	Sulfate
$R-SO_3^-\ M^+$	Sulfonate
	Benzenesulfonate

Most of these ionic surfactants have a single tail and a single headgroup. However, it is possible to synthesize surfactants having multiple tails or headgroups. The Gemini (dimeric) surfactants consist of two hydrophobic tails and two hydrophilic headgroups covalently attached by a hydrophilic or hydrophobic spacer.[11,12] The properties of these surfactants are very different from those of the corresponding conventional surfactants and are strictly dependent on the spacer, whose nature can be very different.[13]

Ionic surfactants are always associated with counterions and their properties are often modified significantly by different counterions.

(iii) *Nonionic Surfactants*

As their name implies, nonionic surfactants contain only electrically neutral headgroups. Unlike ionic surfactants, where hydrophilic portion consists of a small molecular group, the hydrophilic portion of nonionic

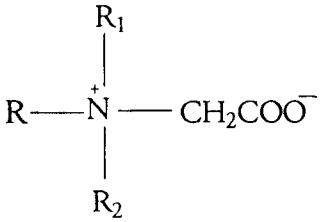
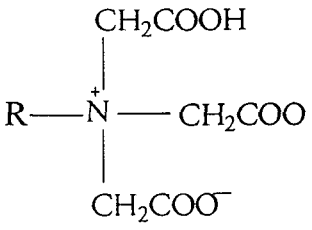
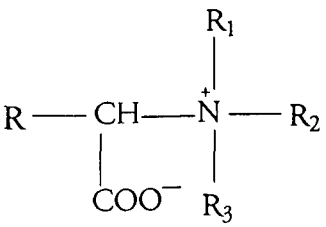
surfactants usually consists of a number of polyoxyethylene oxide groups attached to the long hydrophobic chain. Most prevalent among the headgroups of nonionic surfactants are the oligomers of ethylene oxide. Simple saccharides such as glucose and sucrose are common as headgroups for nonionic surfactants. Alkanolamides such as ethanolamides and diethanolamides, alkylamides, amine ethoxylates, amine oxides (at neutral and alkaline pH), and polyamides are the primary nitrogen-based nonionic surfactant types. The most widely studied class of alkyl ehtylene oxide surfactants, also called ethoxylates, is represented as C_nE_m where n is the number of methylene groups in the alkyl chain and m is the number of ethylene oxide units in the headgroup. Polyethylene glycol tert-octylphenyl ether (Triton X-100) is perhaps the best known member of this class.

Block copolymeric nonionic surfactants have become an important class of dispersants known as polyoxamers and Pluronics. Such block copolymers are often denoted as AB(diblock) or ABA(triblock), where A denotes a hydrophilic (headgroup) block, such as poly(ethylene oxide) (EO), and B denotes a hydrophobic block, such as poly(propylene oxide) (PO) or polystyrene (PS). Commercially available EO/PO copolymeric surfactants generally contain a mixture of homologues of various chain lengths. The chemical structures of some of the hydrophilic groups for nonionic surfactants are

Chemical structure	**Name**
$R-(OCH_2CH_2)_n-OH$	Polyoxyehylene alcohol
$R-COO-(CH_2CH_2O)_n-H$	Polyoxyethylene ester
$R-\underset{\underset{O}{\downarrow}}{S}-R_1$	Sulfoxide

(iv) Zwiterionc Surfactants

The combination of just about any anionic and cationic group in a single amphiphilic molecule confers amphoteric character and is taken to constitute a zwitterionic surfactant. There are two kinds of zwitterionics: pH-sensitive and pH-insensitive. pH-sensitive zwitterionics are ampholytic materials, which show the properties of anionics at high pH's and those of cationics at low pH's. pH insensitive ones are zwitterionics at all pH's (at no pH do they act like merely anionic or cationic). The betaines are very important class of zwitterionics and include alkylbetaines and heterocyclic betaines. The most common zwitterionic surfactants are the carbobetaines and sulfobetaines. The chemical structure of some of the amphiphilic headgroups for zwitterionic surfactants are

Chemical structure	**Name**
	N betaine
	Triglycine
	C betaine

Lecithin, cephalin, and the bile acids are usually classified as biosurfactants. The bile acids and their conjugates have different properties in solution from surfactants with a long alkyl chain.[14-16]

Critical Micelle Concentration

One of the most characteristic properties of amphiphilic molecules is their capacity to aggregate in solutions. Almost from the beginning of the study of the properties of surfactant solutions, it was recognized that their bulk properties were unusual and indicated the presence of aggregates in the solution. The abrupt change in many physico-chemical properties (surface tension, electrical conductance, dielectric constant, viscosity, osmotic pressure, spectroscopic properties, etc.) seen in aqueous solution of the surfactants when a specific concentration is exceeded is attributed to the formation of oriented molecular aggregates (Fig.1.1). The narrow concentration range over which these changes occur has been called the critical micelle concentration (CMC),[17-19] and the molecular aggregates that form above the CMC area are known as micelles. Below the CMC surfactants are present as monomers. Above the so - called CMC, additional surfactant exists in the form of aggregates or micelles which are in equilibrium to the monomers.

Several definitions of CMC have been proposed.[20-22] Philips[23] defined the CMC as the concentration corresponding to the maximum change in the gradient of a solution property (ø) versus concentration (c) curve and is represented as

$$(d^3ø/dc^3)_{c=cmc} = 0 \qquad (1.1)$$

This definition has now been widely accepted.[24-26] A version of this

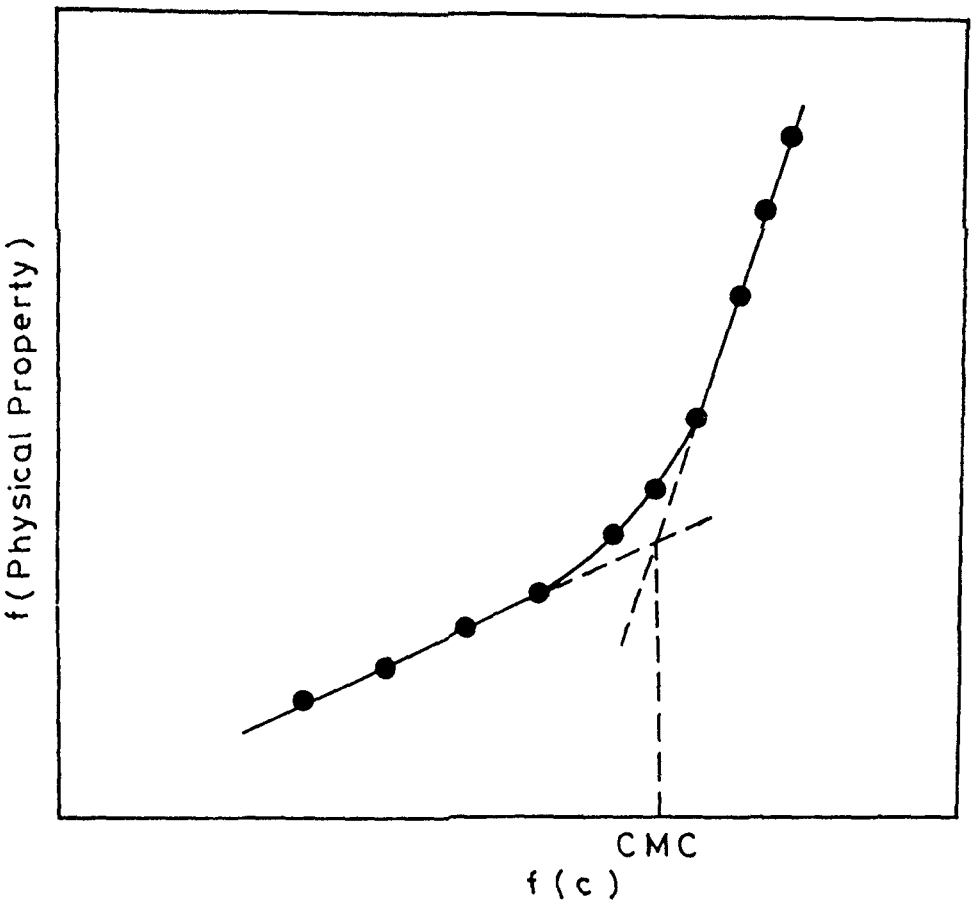


Fig. 1.1 : Change in physical property as a function of surfactant concentration (c).

definition given by Hall[27] uses the chemical potential of the solvent, instead of ø, and is applicable to multicomponent systems.

Many investigators have developed empirical equations relating the CMC to the various structural units in surfactants. Thus, for homologous straight-chain ionic surfactants (soaps, alkanesulfonates, alkylsulfates, alkylammonium chlorides, alkyltrimethylammonium bromides) in aqueous medium, a relationship between the CMC and the number of carbon atoms n in the hydrophobic chain was found as

$$\log c_{cmc} = A - Bn \qquad (1.2)$$

where A is a constant for a particular ionic head at given temperature and B is a constant $\approx 0.3 (= \log 2)$ at 35 °C, for the ionic types mentioned above.

CMC can be determined by different techniques. Just about any experimental probe sensitive to the state of surfactant aggregation is useful for determination of CMC values. Popular techniques include surface tension, turbidity, self-diffusion, conductivity, osmotic pressure, solubilization, surfactant selective electrodes, fluorescence methods, etc. Nearly all of these methods involve variation of measured property as a function of surfactant concentration or as a function of the logarithm of surfactant concentration. The CMC is deduced as a break point. Electrical conductivity measurements are useful for studying micellization of ionic surfactants and are easily applied over wide temperature intervals. As micellization commences, the mobility of the aggregated surfactant structure is less than that of "monomeric" surfactants, so that the increase in conductivity with increasing surfactant concentration is reduced on a surfactant - equivalent basis. The intersection of asymptotic regions then

yields an estimate of CMC. A useful compilation of all methods used together with thousands of CMC values has been produced by Mukerjee and Mysels.[18] The CMC depends on the solution properties employed in the determination and, therefore, differs with method to method. For this reason, measured CMC values define a narrow concentration range. The CMC values obtained from the solution properties mainly due to a monomeric surfactant contribution are found to be less than those due to a surfactant micelle contribution.[28-30] For example, the CMC value obtained from surface tension measurements is less than that obtained from turbidity.[28] In the literature, however, CMC's have been presented as definite concentrations.[29,30] Some changes of colligative properties had been found to take place at higher surfactant concentration far above the CMC; this point was named the second CMC[31] or postmicellar transition. CMC values for commonly used surfactants range from about 10^{-4} to 10^{-2} M.[32,33]

Normal Micelles

In 1920 MacBain and Salmon proposed the existence of micelles.[34] It was Hartley[35] who made the pioneering contributions to the understanding of the micelle. Hartley micelle is described as having linear chains arranged radially, as in the spokes of a wheel.

Micelles are not fixed entities. They are highly dynamic transient species, in which surfactant monomers rapidly join and leave micelles. Thus, in an aqueous surfactant solution, micelles break and reform at a fairly rapid rate, in the range of milliseconds.[36-38] At equilibrium, the number of micelles formed in a given time is equal to the number of micelles disintegrated in the same time period. There are two relaxation

times associated with the micelles: the shorter relaxation time (ι_1), generally of the order of microseconds, relates to the exchange of surfactant monomers between the bulk solution and micelles, whereas the longer relaxation time (ι_2), generally of the order of milliseconds to seconds, relates to the dissolution of a micelle after several molecular exchanges.[39] It has been proposed that the lifetime of a micelle can be given by $N\iota_2$, where N is the number of monomers forming a micelle.[40] A large value of ι_2 represents high stability of the micellar structure.

The structure of micelle in aqueous medium, at concentrations not too far above the CMC, can be regarded to be roughly spherical with an interior region containing the hydrophobic part of the surfactant molecules (known as core) of radius approximately equal to the length of a fully extended hydrophobic chain, surrounded by an outer region containing the hydrated hydrophilic groups and bound water.

Stigter and Mysels[41] suggested that the micellar surface is rough, and Stigter[42] placed the hydrocarbon core-water interface at 0.4 to 1.2 Å from the center of the α-carbon atoms of hydrocarbon chains. Furthermore, on the basis of nuclear magnetic resonance (NMR) studies, it has been proposed that the hydrocarbon tails do not penetrate into the water across the micellar interface and that the first segments of the chains are nearly *trans* whereas the end segments have a conformation similar to that of a liquid hydrocarbon.[43] In other words, the penetration of water into the hydrocarbon core must be very small, certainly less than one water molecule per surfactant molecule. The hydrocarbon core is virtually devoid of water, but NMR data suggest that substantial water/hydrocarbon contact occurs at the core interface.[44]

The nature of micelles has been greatly clarified owing to recent progress in such research techniques as NMR, electron paramagnetic resonance (EPR), neutron scattering, and quasielastic scattering. A vast body of information on the structure of surfactant solutions is available in the literature.

An ionic micelle formed in polar solvents such as water generally consists of three regions (Fig. 1.2) : (i) The interior or core of the micelle which is hydrocarbon like as it consists of hydrocarbon chains of the ionic surfactant molecules, (ii) Surrounding the core is an aqueous layer known as the Stern layer. The Stern layer constitutes the inner part of the electrical double layer. It contains the regularly spaced charged headgroups and 60-90% of the counterions (the bound counterions). The headgroups are hydrated by a number of water molecules. One or more methylene groups attached to the headgroups may be wet. The core and the Stern layer form the kinetic micelle. (iii) The outer layer is a diffuse layer and contains the remaining counterions and is called the Gouy-Chapman layer that extends further into the aqueous phase. The thickness of this layer is determined by the (effective) ionic strength of the solution.

The surface potentials of ionic micelles are very high (~ 100 mV).[41-45] The water activity at the Stern layer of ionic micelle is not much less than in bulk water.[46] For highly charged ionic micelles the shear surface coincides with the "physical surface" of the micelle within the error of about 1 Å . This means that the local viscosity of water remains constant, at its bulk value, to within 1 Å from physical interface.

Small-angle neturon scattering (SANS) experiments on SDS and other ionic micelles support the basic Hartley model of a spherical micelle.[47-49]

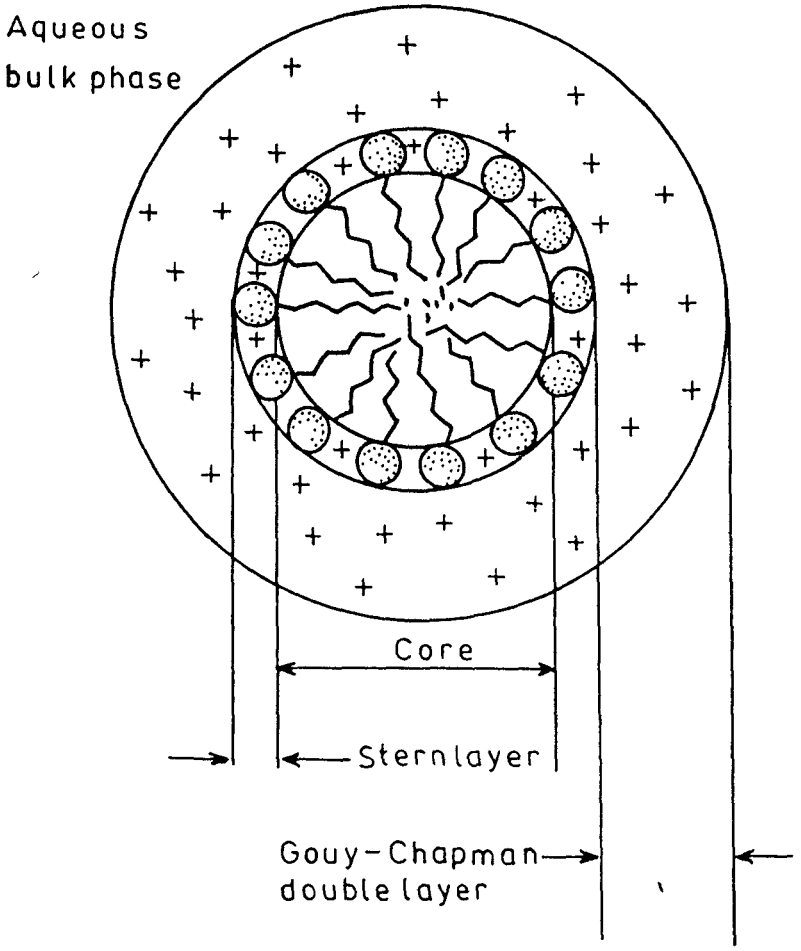


Fig. 1.2 : A two dimensional schematic representation of the regions of a spherical ionic micelle. The counterions (+), the headgroups (O), and the hydrocarbon chains (~~) are schematically indicated to denote their relative locations but not their number, distribution, or configuration.

For nonionic micelles the structure is essentially the same, except that the outer region contains no counterions, but includes coils of hydrated polyoxyethylene chains. Water molecules appear to be trapped on the oxyethylene sites.[50]

Reverse Micelles

Surfactants dissolved in nonpolar solvents form aggregates with tails facing out towards the solvent. The headgroups are in the interior and are effectively shielded from unfavorable interactions with the nonpolar solvent. These aggregates are called the reverse, inverse or reverted micelles (Fig. 1.3). Dipole–dipole[51-53] interactions hold the hydrophilic headgroups together in the core. Such systems usually have small amounts of water present from impurities in the solvent or the surfactant. These water molecules are strongly associated with the headgroups of surfactant.[54] The aggregation properties of surfactants in nonpolar media are often altered markedly by the presence of traces of water or other additives. The current views are that reverse micelles are very small, with aggregation number seldom exceeding 10 due to the lack of strong driving force. It has also been reported[55] that sodium bis(2 - ethylhexyl) phosphate, which is similar in structure to the classical surfactant sodium bis(2 - ethylhexyl) sulfosuccinate (AOT) forms very large rod-like reverse micelles and their size be even larger if water is removed from the nonpolar solution. Long-range electrostatic interactions are the primary force for the formation of giant reversed micelles.

The inner cavity of reverse micelles has been compared with active sites of enzymes. Water in reverse micelles is expected to behave differently from ordinary water because of extensive binding and

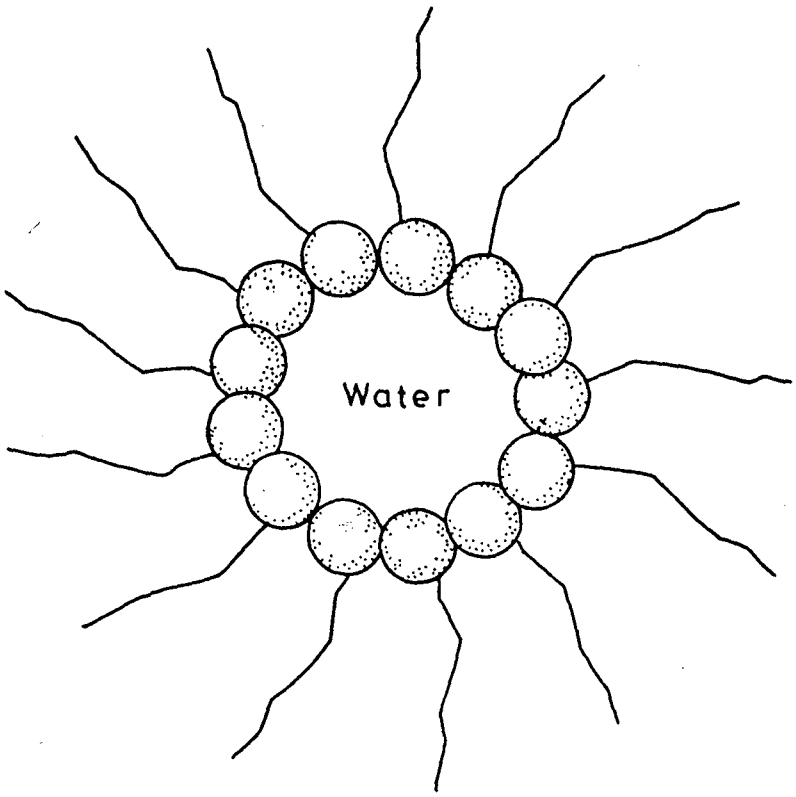


Fig. 1.3 : Schematic structure of a reverse micelle.

orientation effects induced by the polar heads. They are able to solubilize hydrophilic molecules like enzymes and plasmids that are much larger than the original water pool diameter. Such micelles can be considered as novel microreactors whose physical properties can be controlled through the water content.

Mixed Micelles

The incorporation of solubilizates into a surfactant micelle results in the formation of a mixed micelle. As usually used, however, the mixed micelle means a micelle composed of surfactants capable themselves of forming micelles. Thus mixed micellization is a special case of solubilization. The physico-chemical properties of mixed micelles are quite different from those of pure micelles of the individual components. The micellar aggregation number and the association of counterions with micelles change dramatically with composition in mixed micelles, even though mixed micelles of homologous surfactants differing only in hydrophobic chain length are expected to have surface properties similar to those of pure micelles of each surfactant. Most CMC's of binary mixtures fall between the CMC's of the two components, but some fall above[56-59] or below[60-62] this range. Many of the theories concerning the CMC of binary surfactant mixtures have assumed the ideality of each component in the micellar phase.[63,64]

Clint[65] proposed a phase separation model to describe the phenomenon of mixed micelle formation. According to the model, ideal mixing of the surfactants in the micellar phase is assumed which permits calculation of the CMC of the mixed entities in terms of the overall composition of the combined component and the CMC's of the individual surfactants. The ideal mixing theory has been quite successful in

explaining the properties of the surfactants having similar structures but can hardly account for the characteristics of mixed systems of dissimilar structural features. Very recently, Sarmoria *et al.*[66] and Puvvada and Blankschtein[67-69] have developed a molecular thermodynamic model for mixed surfactant systems. Rubingh[60] formulated a theoretical treatment to relate monomer concentration to the micellar composition. However, since the theory of Sarmoria and Puvvada has a more quantitative basis than Rubingh, the former is expected to work better to extract information on mixed surfactant systems over and above micellar composition.

Mixed micellar solutions exhibit some very interesting properties not expected from individual surfactant solutions. The degree of counterion association to an ionic micelle is about 0.7 for monovalent and 0.9 for divalent counterions. When an ionic surfactant is mixed with a nonionic surfactant, the degree of the association falls to zero as mole fraction of nonionic surfactant in the micelle increases.[70,71] This is particularly evident for mixtures of anionic and nonionic surfactants of the polyoxyethylene type, because of the strong interaction between the anionic headgroup and the ethylene oxide group. Various papers have also been published that treat surfactant mixtures from the viewpoint of foam stability,[72] gel filtration,[73] surface adsorption on fibres,[74] NMR,[75] light scattering,[76,77] excess entropy,[78] etc.

Micellization in Nonaqueous Solvents

Micellization of ionic surfactants in nonaqueous polar solvents has been investigated by numerous authors.[79-84] Formamide,[85] hydrazine,[86] glycerol[87] and ethylene glycol[88] allow the surfactant aggregation into micelles. The experiments conducted on formamide[89,90] and ethylene

glycol[91] have shown that the micellization is much less cooperative than in water. Thus micellization process is analogous to that of short chain surfactants in water. The spherical micelles in formamide are smaller than the corresponding ones in water, and they are more charged.[92] In highly polar nonaqueous solvents, such as N - methylformamide, and N, N - dimethylformamide, it appears that the driving force for micellization is mainly entropic[93] (i.e., the tendency of the lyophobic group to transfer the solvent environment to the interior of the micelle). Micelles can also be formed in solvents like acetonitrile, acetone, dimethylsulfoxide, as well as 100% H_2SO_4, D_2O and sol - gel systems.[94-98]

Theories of Micellization

Theoretical treatment of micelles depends on whether the micelle is regarded as a chemical species or as a separate phase. The mass action model, which has been used ever since the discovery of micelles, takes the former point of view,[99-102] whereas the phase separation model regards micelle as a separate phase,[103-105] The mass action model requires knowledge of all the stepwise association constants from monomers to micelles, a requirement difficult to fulfill. This model, therefore, has such defects as the assumption that the micelle aggregation number N is monodisperse (in spite of its actual polydispersity) or the fact that some numerical values for micellization constants are assumed[106,107] when estimating the dispersion of micellar size. The phase separation model, on the other hand, is based on the assumption that the activity[108-111] of a surfactant molecule and/or the surface tension[112-114] of a surfactant solution remain constant above the CMC. In reality, neither quantity remains constant so this model is also not strictly correct. Hill[115] developed the thermodynamics of small systems and also applied it to the

aggregation of solutes. This theory serves as a bridge between the mass-action and phase-separation models. Hall[116] has done further development. In any case, the nature of ionic micelles has been made clearer from the studies of the activity of both surfactant ions[117,118] and counterions[119,120] owing to development of new electrochemical techniques.

Micelle formation takes place by the aggregation of monomeric surfactant molecules dispersed in a solvent. Aggregation is opposed by both an increase in electrostatic energy (for ionic surfactants) and a decrease in entropy due to aggregation. These unfavorable conditions suggest that micellization is associated with an energy decrease resulting from the condensation of hydrophobic groups (hydrocarbon or fluorocarbon chains) of surfactant molecules into a micellar aggregate. What is the mechanism that causes the energy decrease on the condensation of alkyl chains as a liquidlike hydrocarbon core from dispersed monomers in aqueous medium? Generally, a spontaneous condensation of dispersed solute species in a solution by the van der Waals interaction is accompanied by a decrease in both entropy ($\Delta S < 0$) and free energy ($\Delta G < 0$). However, the entropy change is always positive for the transfer of hydrocarbon from an aqueous environment at infinite dilution to a liquid hydrocarbon phase.

An explanation for this increase involves the peculiar property of water as a solvent. Water molecules in the liquid state have structure of hydrogen bonds similar to that of ice, and the cavities in the structure are large enough to accommodate hydrogen chains. The water molecules display equilibria for the formation and destruction of hydrogen bonds with a life time of 10^{-12} s, and movement of free water molecules takes place by stepwise jumps through the cavities. Thus, occupation of a cavity

by hydrophobic solute hinders the movement of free water molecules which therefore remain stationary for longer periods. In other words, the water molecules surrounding a hydrophobic solute become ordered than bulk water molecules.

Frank and Evans[121] introduced the idea that water molecules form "icebergs" around nonpolar solutes. Nemethy and Scheraga,[122] on the other hand, used the term "increased ice-likeness" to characterize the entropy change. Ben-Naim[123] also suggested a shift into the direction of the "better order" form of water molecules upon introduction of a noble gas. According to all these concepts the water molecules become more ordered around the hydrophobic solute, with an increase in hydrogen bonding in this region. These models can account for the negative enthalpy and entropy of solution. In other words, the favorable free energy for transfer of a nonpolar solute from an aqueous environment to hydrophobic environment arises from a large positive entropy associated with the disordering of the water molecules in the vicinity of nonpolar solutes. Such interaction between a nonpolar solute in water molecules is termed as the hydrophobic interaction or hydrophobic hydration, and the condensation of the nonpolar solutes by the hydrophobic interaction is conventionally called the hydrophobic bond.[124,125]

By analogy to the above discussion, the driving force for micellization results from the transferring of nonpolar surfactant chain from an ordered aqueous environment to the hydrocarbon-like environment of the micelle interior, even though a larger negative entropy would otherwise have been expected for the transfer of surfactant molecules and counterions from aqueous solution to the confines of a small molecule.

A further insight into the mechanism of micelle formation is provided by data for cationic surfactants in various non-aqueous solvents. All these solvents, even aprotic ones, were chosen as they have high dielectric constants and high cohesive energy densities, just like water. All the solvents that have multiple hydrogen - bonding capability allow micelle formation while the aprotic solvent 3 - methylsydnone does not, even though its cohesive energy density and dielectric constant are comparable with those of formamide (that allows micelle formation) for example. Evans[126] concluded that multiple hydrogen bonding capability in the solvent is a necessary prerequisite for surfactant self-assembly.

The formation of micelles by ionic surfactants is ascribed to a balance between hydrocarbon chain attraction and ionic repulsion among charged headgroups. For nonionic surfactants, however, hydrocarbon chain attraction is opposed by the requirements of the hydrophilic groups for hydration and space.

Therefore, the micellar structure is determined by equilibrium between the repulsive forces among hydrophilic groups and short-range attractive forces among hydrophobic groups.

Aggregation Number

One of the most fundamental parameters defining a micelle is the aggregation number (N). The average number of monomers in a micelle in a given population distribution or simply the number of monomers making up a micelle, is known as the aggregation number and is typically 30 - 200 in water. The value of aggregation number contains information on the micelle size and shape. It is affected by different factors such as the nature of the surfactant, temperature,[127-130] type and concentration of added

electrolyte,[128,131-133] organic additives,[134-137] etc. As a rule, in aqueous medium, the greater the "dissimilarity" between surfactant and solvent, the greater the aggregation number. Thus, aggregation number appears to increase with increase in the hydrophobic character of the surfactant: increase in the length of hydrophobic group, decrease in the number of oxyethylene units in polyoxyethylenated nonionics, increase in the binding of the counterions to the micelle in ionics. An increase in the temperature appears to cause a small decrease in the aggregation number in aqueous medium of ionics. For nonionic surfactants, it increases fairly rapidly.[138-140]

Micellar aggregation number decreases monotonously with rising pressure for nonionic surfactants,[141,142] although the number for ionic surfactants passes through a minimum at around 1000 atm. Aggregation number of ionic micelles is reported to increase[143-146] by the addition of electrolytes. It also increases with surfactant concentration and for sodium dodecyl sulfate (SDS) it is reported[147,148] that the change with surfactant concentration (c) can be represented by the expression

$$N = k_1 c^r \qquad (1.3)$$

where k_1 is a constant approximately equal to 200 and r = 0.25. Expression for N similar to equation (3) has been found to hold good for cetyltrimethylammonium chloride (CTAC) and acetate surfactants.[149]

In polar solvents, such as chloroform or ethanol, either micellization does not occur or, if it does, the aggregation number is very small, presumably because the polar surfactant molecules can dissolve in the solvent without distorting its liquid structure significantly. As might be expected, in these solvents, surfactants have also almost no tendency to adsorb at interfaces.

Some of the important techniques allowing the estimation of aggregation number are sedimentation, SANS, NMR, light scattering, fluorescence quenching, etc.

Factors Affecting the Value of Critical Micelle Concentration

Since the properties of solutions of surface-active agents change markedly when micelle formation commences, a great deal of work has been done on elucidating the various factors that determine the concentration at which micelle formation becomes significant, especially in aqueous media.

Among the factors known to affect the CMC markedly in aqueous solutions are : (i) the structure of the surfactant, (ii) the presence of added electrolyte in the solution, (iii) the presence in the solution of various organic additives, (iv) the temperature of the solution, and (v) pressure.

(i) *Structure of Surfactant*

In general, the CMC decreases as the hydrophobic character of the surfactant increases.

The Hydrophobic Group: A generally used rule for ionic surfactants is that the CMC is halved by the addition of one methylene group to a straight chain hydrophobic group attached to a single terminal hydrophilic group. The presence of branched chains or double bond hinders micelle formation and thus increases the CMC. This is apparent from the equation (2). When the number of carbon atoms in a straight-chain hydrophobic group exceeds 16, however, the CMC no longer decreases so rapidly with increase in the length of the chain and when the chain exceeds 18 carbon atoms it may remain substantially unchanged with further increase in the

chain length. This may be due to the coiling of these long chains in water. A phenyl group that is part of a hydrophobic group with terminal hydrophilic group is equivalent to about three and one-half methylene groups. The replacement of a hydrocarbon-based hydrophobic group by a fluorocarbon-based one with the same number of carbon atoms appears to cause a decrease in CMC. This is explained in terms of the enhanced hydrophobicity.

The Hydrophilic Group: Ionic surfactants have much higher CMC's than nonionic surfactants containing equivalent hydrophobic groups; 12-carbon straight-chain ionics have CMC's of approximately 1×10^{-2} M, whereas nonionics with the same hydrophobic group have CMC's of approximately 1×10^{-4} M. The higher CMC's of ionic surfactants are a consequence of electrical repulsion between ionic headgroups that strongly opposes micelle formation. The more charged groups in the surfactant, the higher the CMC due to increased electrical work required to form micelles.[150,151] Zwitterionics appear to have about the same CMC's as ionics with the same number of carbon atoms in the hydrophobic group. As the hydrophilic group is moved from a terminal position to a more central position, however, the CMC increases. It is because the hydrophobic group seems to act as if it had become branched at the position of the hydrophilic group. For usual type of polyoxyethylenated nonionics, the CMC decreases with decrease in the number of oxyethylene units in the polyoxyethylene chain, since this makes the surfactant more hydrophobic.

The Counterions in the Ionic Surfactants: In aqueous medium the CMC's of ionic surfactants decrease as the hydrated radius of the counterion decreases. Replacing a counterion by one of greater polarizability or higher valence also decreases CMC.[101,152] Thus, for the ionic dodecyl

sulfates, the CMC decreases in the order $Li^+ > Na^+ > K^+ > Cs^+ > N(CH_3)_4^+ > N(C_2H_5)_4^+ > Ca^{++}, Mg^{++}$. When the counterion is the cation of a primary amine, RNH_3^+, the CMC decreases with increase in the chain length of the amine. For cationic dodecyltrimethylammonium and dodecylpyridinium salts, the order of decreasing CMC in aqueous medium is $F^- > Cl^- > Br^- > I^-$.

(ii) ***Electrolyte***

In solutions of increasing ionic strength, the forces of electrostatic repulsion between headgroups of an ionic micelle are considerably reduced, enabling micelles to form more easily, that is, at lower concentration. In other words, addition of electrolyte to ionic surfactants causes decrease in CMC,[153] the effect being more pronounced for anionic and cationic than for zwitterionic surfactants, and more pronounced for zwitterionics than for nonionics. The effect of the concentration of electrolyte on CMC of ionics is given by the following relation

$$\log c_{cmc} = a \log c_I + b \qquad (1.4)$$

where a and b are constants for a given ionic head at a particular temperature and c_I is the total (monovalent) counterion concentration in moles per litre. The depression of CMC in ionic surfactants is due mainly to the thickness of the ionic atmosphere surrounding the ionic headgroups in the presence of the additional electrolyte and the consequent decrease in electrical repulsion between them in the micelle. The effect of weak electrolytes on the CMC of SDS has been studied recently by Esposito et al.[154] Moreover, it has been reported[155] that coions of the added electrolyte also affect the CMCs of ionic surfactants in addition to the effect of counterions.The change in the CMC of nonionics and zwitterionics on the

addition of electrolyte has been attributed mainly to the "salting-out" or "salting-in" (i.e., the effects of ionic size and decrease in dielectric constants) of the hydrophobic groups in the aqueous solvent by the electrolyte, rather than to the effect of the latter on the hydrophilic groups of the surfactant. Electrolytes capable of "salting-out" reduce the CMC of nonionic surfactants while "salting-in" electrolytes increase the CMC.

For nonionics and zwitterionics equation (1.4) does not hold. Instead, the effect is given better by the equation

$$\log c_{cmc} = -k c_s + \text{constant} \quad (c_s < 1) \qquad (1.5)$$

where k is a constant for particular surfactant, electrolyte and temperature and c_s is the concentration of electrolyte in moles per liter.

(iii) *Organic Additives*

Organic compounds affect the CMC either by penetrating into the micellar region, or by modifying solvent - micelle or solvent - monomer interactions. Both increase and decrease of CMC are observed on addition of non-electroytes[156-166] like urea, amides, amino acids, alcohols, carbohydrates, esters, etc. Polar compounds that are believed to penetrate into the inner portion of the core produce only small depressions of the CMC, like hydrocarbons (known to be solubilized in the inner portion of the core) which decrease the CMC only slightly. Addition of propanol or longer chain alcohols promotes micelle formation and lowers the CMC.

Compounds that affect the CMC by modifying solvent - micelle or solvent - surfactant interactions do so by modifying the structure of the water, its dielectric constant, or its solubility parameter (cohesive energy density). Water structure breakers like urea, formamide, and guinidinium

salts are believed to increase the CMC of surfactants in aqueous solutions (the increase of the CMC of ionics by urea is small), because of their disruption of water structure. Materials that promote water structure such as xylose or fructose decrease the CMC of surfactants.[167]

Dioxane, ethylene glycol, glycerol[168,169] and short chain alcohols at high bulk phase concentrations may increase the CMC of ionic and nonionic surfactants because they decrease the cohesive energy density, or solubility parameter of the water, thus increasing the solubility of the monomeric form of the surfactant and hence the CMC. An alternative explanation for the action of these compounds, in the case of ionics, is based on the reduction of the dielectric constant of the aqueous phase that they produce. This would cause increased mutual repulsion of the ionic heads in the micelle, thus opposing micellization and an increase in CMC.

(iv) *Temperature*

The effect of temperature on the CMC of surfactants in aqueous medium is complex. Temperature increase causes decreased hydration of the hydrophilic group, which favors micellization. However, temperature increase also causes disruption of the "structured water" surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range. The CMC of ionic surfactants usually passes through a minimum with increasing temperature. For SDS in water the minimum in CMC occurs around 298 K[170] whereas for hexyl trimethylammonium bromide it occurs at 303 K.[171] For nonionic surfactants, CMC minimum appears to be at 323 K. La Mesa[172] used the reduced variable treatment to explain the temperature dependence of CMC. Muller[173] derived a better analytical

expression in terms of heat capacities of micellization to describe the temperature dependence of CMC. The temperature of minimum CMC for both nonionic and ionic surfactants increases as the hydrophobicity of surfactants decreases.[174] CMCs of alkyltrimethylammonium bromides in water are reported even upto 433 K.[175,176] The position of the minimum has thermodynamic significance. The CMC is a measure of the standard free energy change for micellization and can be written as

$$\Delta G^{\circ}_{m} = - R T \ln (CMC) \qquad (1.6)$$

Therefore, the minimum in CMC represents a minimum in the free energy of micellization.

(v) *Pressure*

Many reports have appeared on the effect of pressure on micelle formation of the ionic[177-182] and nonionic surfactants.[183] With pressure CMC of ionic surfactants increases upto 1000 atm followed by a decrease above this pressure.[184-189] Such behavior has been rationalized in terms of solidification of the micellar interior,[184] increased dielectric constant of water,[185] and other aspects related to water structure.[186] For nonionic surfactants, the CMC value increases monotonously and then levels off with increasing pressure. La Mesa[172] has also discussed the effect of pressure on the CMC.

Packing in Aqueous Assemblies

Amphiphilic molecules dissolved in water over CMC can form various types of aggregates or micelles. Various theoretical approaches have been proposed to interpret data collected from different types of experiments. In one of these approaches the formation of micelles in a

solution of ionic surfactants is assumed to be a stepwise kinetic process in which assemblies of aggregation number N are formed from those having aggregation number N ± 1. Thus, in a way similar to chemical reactions, the process may be described as being in equilibrium in terms of thermodynamics. The chemical potential involved in thermodynamic considerations has its origin in solute/solvent, solute/solute, and aggregate/aggregate interactions. The first two interactions can be expressed by the specific area of the micelle/solution contact surface belonging to one headgroup. The solute/solvent interaction arises mainly from the hydrophobic effect exerted by water molecules on the long aliphatic chain of surfactants, and its contribution is proportional to the specific headgroup area.[22,190,191] The solute/solute interaction in the case of ionic surfactants is of electrostatic nature: its contribution mainly comes from the coulombic repulsion among the headgroups and is somehow inversely proportional to the specific headgroup area.[192-196] The opposite tendency of these two contributions ("opposing forces", introduced by Debye[192]) versus specific headgroup area defines a minimum energy contact surface and with packing constraints determines the micellar size and shape at least for small surfactant concentrations.

According to recent theories,[197,198] at higher surfactant concentrations the aggregate/aggregate interaction plays an increasing dominant role and becomes the size- and shape-determining factor.

The interpretation of the results obtained from thermodynamic analysis requires that thermodynamic quantities be expressed in terms of the molecular parameters of the assumed microstructures. The existence of these microstructures is proven and their proportions are investigated by using different light scattering[199-201] as well as small-angle X-ray[202] and neutron scattering[47,203,204] techniques.

The geometry and nature of the aggregates depend mostly on concentration and type of the surfactant or the surfactant mixture. Also, the presence of electrolyte can have a marked influence on the type and shape of the aggregate.

As the concentration is increased above CMC, the shape of ionic micelles changes in the sequence sperical–cylindrical–hexagonal–lamellar.[205-208] For nonionic micelles, on the other hand, the shape changes from spherical directly to lamellar with increasing concentration.[209,210]

Various micellar aggregates, such as ellipsoidal or rod-like micelles, can form supramolecular assemblies having cubic symmetry. At sufficiently high concentrations, spherical micelles are transformed into rod-like micelles. Cylindrical rods can pack hexagonally in two dimensions to form the normal hexagonal mesophase. This phase is known as middle phase in soap technology and is highly anisotropic. Inverse hexagonal phases form from reverse rod-like micellar assemblies.

Some water-insoluble surfactants that do not form micelles, usually those with two or more hydrocarbon tails, can be suspended in water as vesicles or lamellar liquid crystal phases. Vesicles are closed bilayer structures, which often have several nested compartments, resembling the skin of an onion. Sonication of these systems often gives single compartment structures. As vesicles are generally non-equilibrium structures, a large number of different types of vesicles can be produced. Vesicles made from phospholipids are called liposomes and are important models for biological membranes. Vesicles are much larger than micelles, or microemulsion droplets. They are typically on the order of 50 nm long and 5 nm wide. They are stable upon dilution. Equilibria involving

surfactant monomers are much slower than for micelles. For this reason, water-soluble solutes can be incorporated in the large inner water pools of the vesicles, and they escape only slowly. Photochemically induced electron transfer across vesicle bilayers has been studied extensively.[32,211-212]

Lamellar liquid crystal phases are layered structures composed of interleaved surfactant bilayers and water. The surfactant length defines the bilayer thickness. The specific interactions between the headgroup and water affect the bilayer structural factors such as average chain tilt angles. Such interactions also affect the amount of water that can be incorporated in the polar regions between bilayers. Lamellar aggregates can be formed from delicate mixtures of anionic and cationic surfactants in water or mixtures of ionic surfactants and long-chain alcohols in water[213] or electrolyte solution.[214] Interaction between lamellae may occur, leading to the formation of either unilamellar vesicles (small or large) or multilayered systems (oligo- and multilamellar vesicles, lamellar droplets, or a continuous lamellar phase). The induction of a lamellar arrangement of surfactant molecules by salts finds an important commercial application in liquid laundry detergents.[215-217]

An interesting structure in aqueous surfactant systems is the "sponge" phase.[218] This phase is actually an isotropic solution phase of surfactant in water, in which the surfactant assembles into a bilayer film that divides the continuous aqueous phase into two separable domains, "inside" and "outside". The film has no long range order or regular periodicity, although shear has not been noted to induce flow birefringence.[219]

Surfactant bilayers with a zero mean curvature avoid supramolecular structures with rims. They can avoid rims by the formation of "tubuli".

Such structures can be regarded as unidimensional vesicles. Tubuli has recently been found in equilibrium phases of ternary mixtures of dimyristoylphosphatidylcholine (DMPC), water and the cosurfactant gereniol.[220] Tubuli from perfluoro-surfactants have been observed both by transmission electron microscopy (TEM) and by phase contrast optical microscopy.[221] Tubuli can exist with the chains in the liquid-crystalline and in the crystalline state. These can be both rigid and flexible.

Packing Parameter

The shape of the surfactant aggregate is mainly determined by surfactant packing parameter which is a dimensionless group relating the volume of the hydrocarbon tail of the surfactant molecule (v), the length of the hydrophobic chain (l_c), and the headgroup area (a_h).[22,222] The packing parameter R_P is given by the expression

$$R_P = v/a_h l_c \tag{1.7}$$

The optimum cross sectional area per amphiphilic molecule is observed experimentally by X-ray diffraction of bilayer systems, while the volume and length of the hydrocarbon tail may be calculated following Tanford[128]

$$v = (27.4 + 26.9\ n)\ Å^3 \tag{1.8}$$

$$l_c = (1.5 + 1.265\ n)\ Å \tag{1.9}$$

Considering the geometric dimensions, the volume and the surface area of each associated structure yield critical conditions for the formation of different shapes (Fig. 1.4). These shapes may be related to assembly structural types with characteristic curvatures. For $R_P \leq 1/3$ the critical packing shape is that of a cone with base area a_h. Self-assembly of such

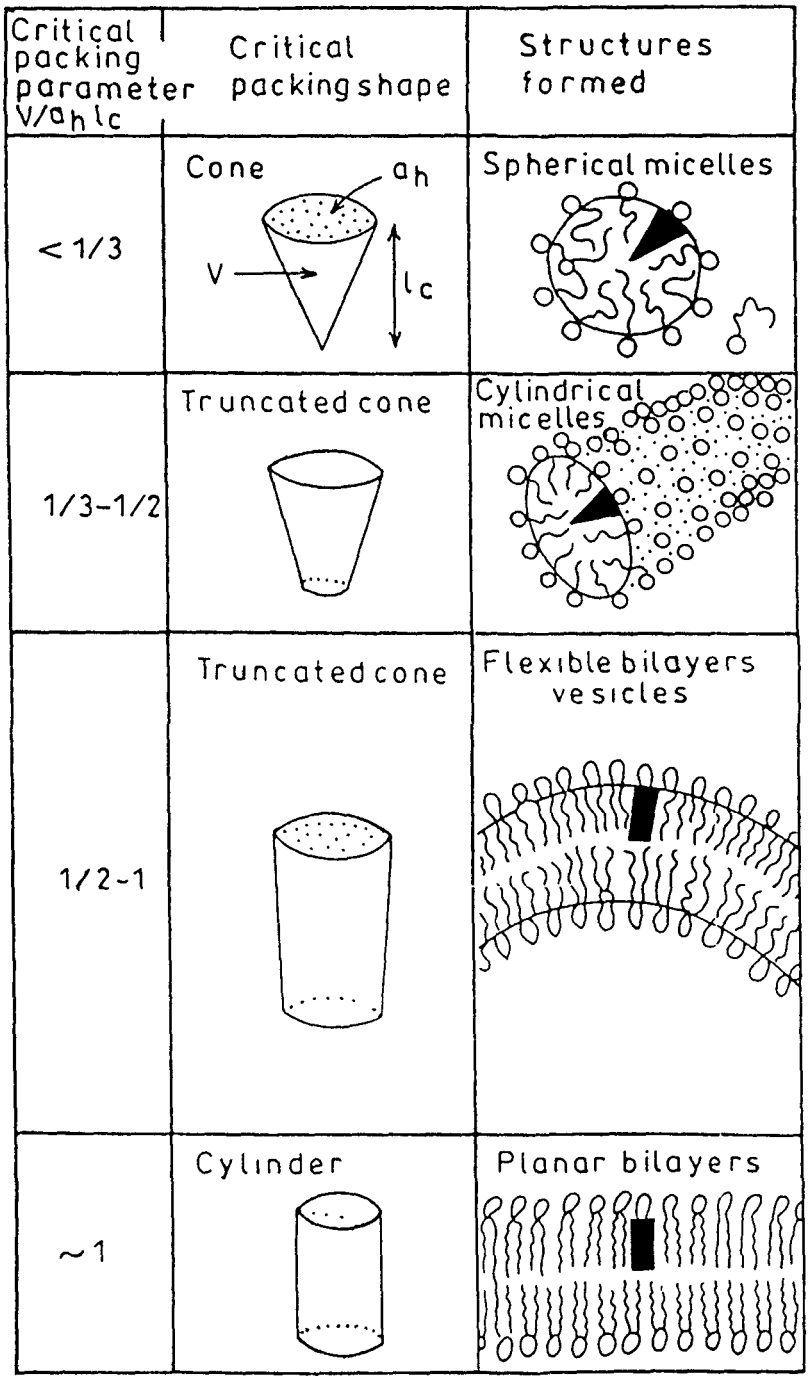


Fig. 1.4: The packing parameter of surfactant molecules and the various structures they form in aqueous solutions.

cones generally leads to spheroidal micellar structure or to globular hemimicelles on surfaces. SDS, dodecyltrimethylammonium bromide (DTAB) and single chain lipids with large headgroups tend to form spherical micelles. Spherical SDS micelles have a radius of about 2.5 nm and each surfactant molecule occupies approximately 60Å^2 of surface.[41]

When this parameter is in the range 1/3 < Rp < 1/2 the critical packing shape is that of a truncated cone. Such cones may be assembled to form rod-like structures such as cylindrical micelles. Surfactants such as SDS and CTAB at sufficiently high ionic strength form rod-like micelles.

Highly truncated cones are obtained as critical packing shapes for 1/2 < Rp < 1 where flexible bilayers are formed such as found in vesicles and liposomes. These shapes are typically obtained from double chain surfactants such as lecithin, AOT and dialkyldimethylammonium salts.

Cylindrical critical packing shapes with $R_P \approx 1$ yield planar bilayer assemblies. Multilayer planar bilayers are routinely produced in device fabrication research[223] and in new applications of surfactant-mediated electrocatalysis.[224]

As the critical packing shape is distended further to yield inverted truncated cones with $R_P > 1$ inverted spheroidal micelles are obtained. Most doubly chained surfactants with measurable solubility in water and oil, such as AOT and didodecyldimethylammonium bromide (DDAB) form these inverted micellar structures in isotropic reverse micellar and microemulsion phases. These same surfactants also form inverted anisotropic liquid crystalline phases.

It may be mentioned that the effective headgroup area a_h can be altered by addition of salt to the micellar solution or by changing the

solution temperature and this results in changes in micellar shape.[146,225-227] The addition of an electrolyte to the ionic micellar solution, for example, screens the coulombic repulsion between the headgroups and this modifies the value of a_h. The value of a_h for nonionic surfactants changes on heating because of dehydration of hydrophilic tails. SANS experiments have shown that micellar structures change on addition of salt or with a change in temperature.[228-232]

Counterions (e.g., Na^+, K^+, etc.) decrease the effective headgroup area (increase in packing parameter) by neutralizing the charge on the micellar surface and this results in transformation of spherical to cylindrical ones. The effectiveness of the counterions in charge neutralization depends on the relative affinity of these ions to the micelle or the water. It seems that the affinity of alkali ions to water decreases as we go from Na to Cs. A smaller hydrated counterion results in a large micellar growth. It may be noted that though the sizes of the hydrated K^+ and Cs^+ ions are similar, the water of hydration is more in K^+ as the bare ionic size of K^+ is smaller than that of Cs^+.

Effect of Temperature on the General Features of Surfactant Phase Behavior

A useful method for describing surfactant phase behavior is in the form of a phase diagram. As we move away from the familiar region of the micellar solution there are three areas in the diagram that have features of most interest and these are illustrated schematically in Fig. 1.5. First, if the solution is cooled, a temperature below which the surfactant is not really very soluble at all is reached, known as the *Krafft temperature*.[233,234] If, on the other hand, the temperature is raised, especially for nonionic surfactants or those with some nonionic polar

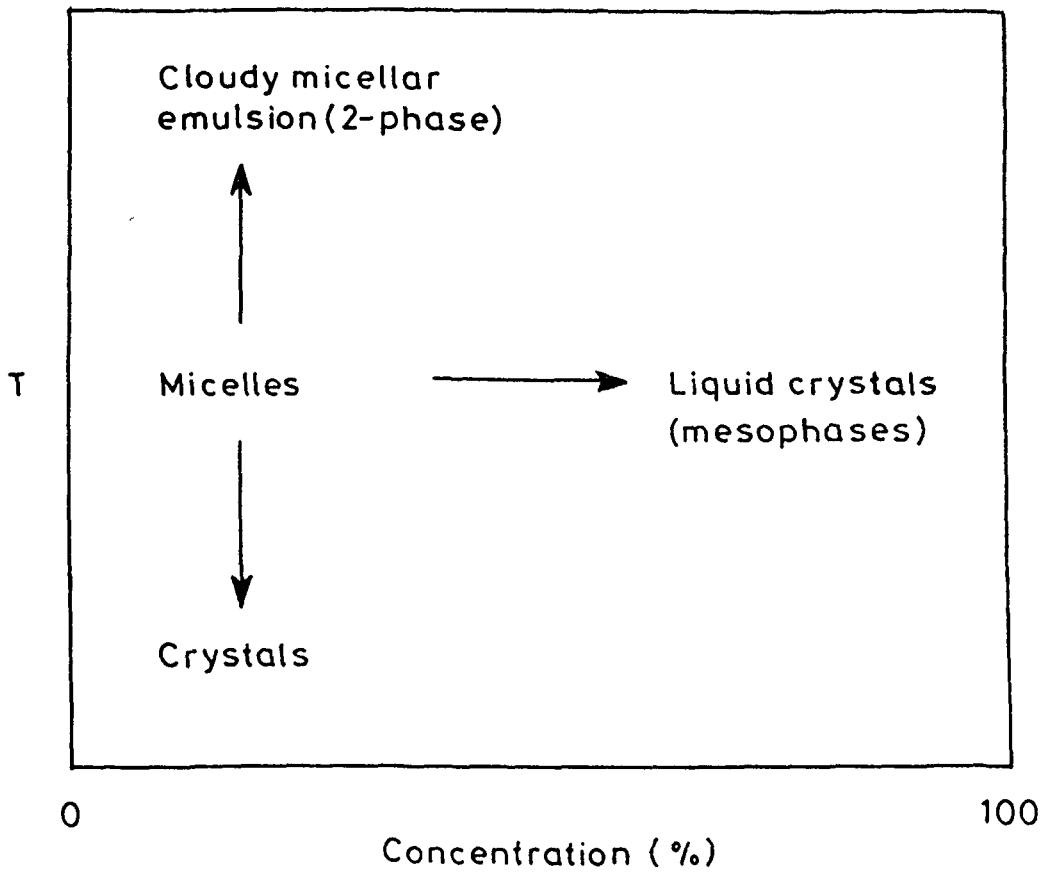


Fig. 1.5: Schematic temperature (T) – concentration phase diagram illustrating the types of surfactant aggregates encountered by moving away from the micellar region.

groups, a two - phase region is encountered, above what is known as the *cloud point* (CP)[235-237] where two liquid (micellar) phases are in equilibrium. Finally, if we increase concentration at ambient temperature, one starts to encounter, usually at surfactant concentrations above about 40% by weight, a series of mesomorphic phases sometimes called liquid crystalline phases. Each of these three regions embodies some fascinating physical chemistry, but under the present topic, solution behavior of the middle region will be commented.

Nonionic surfactants cannot withstand elevated temperature and become insoluble manifesting turbidity, called 'clouding'. The phenomenon is an indication of their instability in solution. The threshold temperature for this state is called the CP. The first manifestation of this phenomenon is the appearance of turbidity throughout the bulk of the solution. Above this temperature, the solution separates into two phases: one, very small in volume, composed almost totally of the surfactant with a small amount of water (referred to as surfactant-rich or *coacervate* phase), and the other, the bulk aqueous solution (aqueous phase) in which the surfactant concentration will be approximately equal to its CMC. The cloud point phenomenon is reversible and when the temperature falls below cloud point, a single phase appears again. The value of the CP depends on the structure of the surfactant molecule, the presence of additives, and the concentration of the surfactant.

Binary liquid mixtures that display partial miscibility exhibit critical solution temperatures (CST) or consolute temperatures. CST's are of two kinds: upper critical solution temperature (UCST), above which the liquid pair is completely miscible and below which phase separation occurs, and lower critical solution temperature (LCST) below which two components

are completely miscible while above it the two components become partially miscible and form two separate phases.

One may find from the literature that there are two classes of surfactants and the temperature effect on the solution behaviors of each class are in sharp contrast. The first class is the nonionic surfactants, the micellar size of which increases (or at least does not decrease) with increase in temperature. Such systems always have cloud point properties.[238-247] This behavior has been attributed to dehydration of the hydrophilic group of the surfactant with increasing temperature.[241] The absence of long range electrostatic interactions between aggregates and the decreasing hydration of nonionic headgroups with increasing temperature result in the spontaneous phase separation.

The ionic surfactants belong to the second class in which the cloud point phenomenon is rarely observerd.[242] Until recently it was thought that this type of behavior was not possible in binary ionic surfactant — water solutions due to the large electrostatic repulsions between the aggregates.

High concentrations of salts can cause ionic surfactant solutions to separate into immiscible surfactant - rich and surfactant - poor phases.[245] This phenomenon has been investigated since the 1940s and was first observed for mixtures of the cationic surfactant Hyamine 1622 with salts such as potassium thiocyanate (KSCN) and potassium chloride (KCl).[246,247] The phase separation is typically of the upper consolute type, i.e., it occurs on cooling below a characteristic temperature, which, in turn, increases with salt content. Later on, few more studies on ionic surfactant – salt combinations were performed to show CP phenomenon (lower consolute type).[242-244] Appell and Porte[242] found cloud points at

high concentrations of sodium chlorate ($NaClO_3$) in aqueous solutions of either cetyltrimethylammonium bromide (CTAB) or cetylpyridinium bromide (CPB). In a later study, Warr and co-workers[243] showed that quaternary ammonium surfactants with tributyl headgroups exhibit cloud points in binary aqueous solution. Adding salt to these surfactant solutions lowers the cloud point temperature. Warr *et al.*[243] advanced a mechanism involving hydration shells to account for cloud points, whereas Appell and Porte[242] interpreted the clouding of CPB/$NaClO_3$ mixtures as being analogous to the phase separation of polymers in a poor solvent.

Recently, Raghavan *et al.*[248] has reported the clouding behavior in ionic surfactants in presence of salts with hydrophobic counterions. The plausible hypothesis given is that the binding of hydrophobic counterions promotes micellar branching. As free micellar ends are incorporated into a branched network, the viscosity of the solution drops, and the entropic attraction between junction eventually causes phase separation. Interest has been focussed on the possibility that upper or lower critical points could occur within ordered liquid crystal phases. An upper consolute loop within a lamellar phase has been reported for binary anionic[249] or cationic[250] surfactants in water. However, lower consolute loops are much rarer. Some ionic surfactants are reported[243] to undergo phase separation without the addition of electrolyte, and their micelles remain spherical or near spherical throughout their region of stability. The parameters, which govern the phase equilibria and particularly the lower consolute behavior of ionic surfactant solutions, have been detailed.[244]

For ionic surfactants, the electrostatic interactions predominate and it has been shown that quantitative prediction of the appearance of phase

equilibria is possible by taking only ionic interactions between the end groups and counterions into account.

It has been shown[251,252] that certain mixed surfactant solutions clouded in two stages, first becoming faintly turbid (preclouding) and then fully clouded at a higher temperature. Older literature references to this phenomenon were limited to brief reports of solution conditions referred to as a "double cloud point", or an "apparent cloud point".[253] Using turbidity as a delineator of clouding, a stable colloidal phase which existed over a broad temperature range between the homogeneous solution and the macroscopically clouded suspension was observed. This phenomenon was first noted by Maclay[253] in 1956 and examined by Nishikido *et al.*[254] in 1977. A tentative mechanism for preclouding, which may be useful as a basis for further deliberations on the phenomenon, can be presented as follows. An assembly of nonionic micelles in a solution containing a minor proportion of an ionic surfactant will include both charged and uncharged aggregates, with the former incorporating one or more ionic species. As the temperature is raised, pairs of micelles coalesce to form larger bodies, but each such event is limited to either two uncharged micelles or a charged micelle and an uncharged micelle. The coalescence of two charged micelles is explicitly excluded because of mutual repulsion. This process inevitably leads to an assembly of aggregates that are all charged and therefore coalesce no further, constituting a relatively stable suspension. The size range of the particles in such a system is dictated by the relative proportions of nonionic and ionic surfactant, and the resulting suspension will be colloidal only for certain compositions. These solutions correspond to the ones that undergo preclouding.

Lower consolute behavior in surfactant solutions is well documented in two situations: nonionic surfactants, either polyoxyethylene alkyl ethers or alkyldimethylamine oxides in water,[255,256] and cationic surfactants[242] in concentrated electrolyte solutions. The nonionic polyoxyethylene systems have been investigated in far greater detail than the ionics, but both classes exhibit several common features. Classical light-scattering studies have been interpreted as indicating a rapid increase in micellar aggregation number, with long cylindrical micelles being formed.[139] However, other interpretation of this phenomenon, and of SANS data, suggest that only a modest growth (if any) in micelle size occurs but that intermicellar interaction increases markedly as the two-phase boundary is approached.[257]

From the thermodynamic point of view it is suggested that the primary reason for the CP behavior in nonionics is that the water around the polyoxyethylene chain is more structured than bulk water, i.e., it has a lower enthalpy and entropy than bulk water (the fact that a LCT exists actually implies that the heat of mixing of polyoxyethylene with water below the LCT is exothermic). When the hydration shells of two neighboring chains overlap, water is forced to leave these shells and the enthalpy and entropy of the system increases. At sufficiently high temperature, the entropy gain in this destructuring of water is high enough to overcome the repulsive enthalpy contribution and the loss in entropy due to increased concentration. Phase separation then occurs. It can therefore be concluded that the increased attraction leading to phase separation is a consequence of a strong entropy dominance in the force.

Micellar Growth and Viscoelasticity in Surfactant Solutions

The properties of micellar solutions, such as CMC, aggregation number, micelle size and shape, etc., depend on the balance between "hydrophobic" and "hydrophilic" interactions. For ionic surfactants this balance can be modified in several ways, i.e., by salt addition, counterion complexation, addition of polar amphiphilic substances that can be solubilized into the micellar headgroup region, change of the solvent, or change of the "structure" of the solvent itself. The growth of micelles from minimum aggregation number, approximately spherical micelles, to rod-like spherocylinders has been of great experimental and theoretical interest.[258-260]

For solutions of ionic surfactants the micelle size and shape may show abrupt changes when the concentration increases to a value much higher the CMC (called second CMC)[261] or when the concentration of added salt has reached a certain threshold value. The presence of salt ions near the polar heads of the surfactant molecules decreases the repulsion force between the headgroups. A reduction in the repulsion makes it possible for the surfactant molecules to approach each other more closely and form larger aggregates, which requires much more space for the hydrophobic chains. Because a spherical micelle has a small volume, it must change into the rod-like micelle to increase the volume/ surface ratio. The existence of rod-like micelles was inferred from experiments of light scattering[262] and confirmed by direct observation under the electron microscope for some systems.[263,264]

Theoretical studies showed that worm-like micelles are long and flexible and that they undergo transformations on relatively short time scales.[265] This was confirmed by negative staining[266] and *cryo-*

transmission electron microscopy (*cryo*-TEM).[267] The flexibility of rod-like micelles of ionic surfactants is determined by their surface charge density and the thickness.

Certain cationic surfactants are known to exhibit viscoelastic behavior in presence of salts/acids.[268-271] The term viscoelasticity denotes the simultaneous coexistence of viscous and elastic properties. The solutions have very high viscosities. Viscoelasticity can, for example, be seen by simply swirling the solution and visually observing the recoil of air bubbles trapped in the solution after the swirling is stopped. The viscoelasticity is manifested in a number of other properties as, for example, a non-Newtonian viscous behavior[272] and a flow - induced optical anisotropy.[273]

Usually the viscoelastic behavior is observed when a third component is added to a rather dilute (<1% w/w) aqueous solution of an ionic surfactant. Viscoelastic behavior shows a considerable chemical specificity both with respect to counterions[268] and additives.[274,275] Gravsholt[268] was the first to observe that in case of CTAX systems, the 4 - chlorobenzoate anion (4ClBen) induced viscoelasticity, while the isomeric 2-chlorobenzoate anion (2ClBen) did not.

Since many viscoelastic micellar solutions in fact show monoexponential stress relaxation functions, there must be an additional process for relaxation available, namely reversible scission of the micellar threads (with a characteristic time constant for breaking). The micellar solutions are accordingly referred to as being analogous to solutions of "living" polymers.

The phenomenon is best demonstrated by mixing two equal volumes of a 50 mM CTAB solution with a 30 mM solution of sodium salicylate

(NaSal) both of which are Newtonian.The effect can also be observed at other surfactant /salt ratios and other concentrations but one can easily observe the phenomenon at this ratio.[276]

The same behavior can be observed on mixing other surfactants. Table 1.1 lists some surfactants which are suitable for preparing viscoelastic solutions.

Table 1.1: Surfactant Systems Exhibiting Viscoelastic Properties.

Surfactant	Added Compound
Cetylpyridinium chloride	Na-salicylate
Cetyltrimethylammonium bromide	Na-salicylate
Cetyltrimethylammonium chloride	NaSCN
Cetyltrimethylammonium chloride	2-Aminobenzenesulfonate
Cetyltrimethylammonium chloride	Perfluorobutyrate
Cetyltrimethylammonium chloride	4- Methylsodium benzoate
$CxF_{17}SO_3Na$	$(C_2H_5)_4$ NOH
$C_9F_{19}CO_2Na$	$(CH_3)_4$ NOH
Tetradecyldimethylaminoxide	Sodium dodecyl sulphate
Tetradecyldimethylaminoxide	C_7F_{15} CO_2 Na
$C_{14}H_{29}N^+$ $(CH3)_2$ - CO_2^-	Sodium dodecyl sulphate
Cetyltrimethylammonium bromide	Chloroform
Cetyltrimethylammonium bromide	1- Methyl naphthalene
Cetylpyridinium chloride	4- Propylphenol

What causes viscoelasticity in these systems? In surfactant solutions exhibiting normal behavior, globular micelles are present; these are

charged and are surrounded by an electric double layer. The mean distance between neighboring micelles is much greater than their size and the solutions are in this sense dilute and behave like dilute dispersions. With the salt addition, formation of rod-like micelles takes place. These rods grow rapidly in size until their lengths are greater than the intermicellar distance and the system can now be called semidilute. In this situation the rods can - like polymer chains - form entanglements, or they actually may even form a three-dimensional network because the system strives to achieve a state in which globular micelles and thus also end caps of the rods are no longer present. Network is a temporary one which is continuously broken and reformed by Brownian motion. Cates and co-workers[277] have developed the theoretical framework needed to describe the micellar dynamics in the semidilute regime, dynamics which manifest themselves in the solution's rheological behavior.

While a viscoelastic surfactant system can be built up by mixing an additive to a micellar solution, it is likewise possible to destroy the viscoelastic properties again by the addition of a third component.[278] If too much hydrocarbon or water is solubilized, the network of long cylindrical aggregates is transformed into globular structures. The transition can easily be monitored by light - scattering measurements.

The observed trasformation can be explained as follows: The hydrocarbon molecule with no polar headgroup is solubilized in the interior of the rod-like micelles; the transformation of the rods can only be understood in terms of a simple geometrical model. In the rods the surfactant headgroups are rather tightly packed. With the solubilization of the hydrocarbon the cross- section of the rods begins to increase. A soon as the inner core reaches a size which allows the packing parameter to be

the same as in globular micelles,[279] the system undergoes transformation because the higher number of globular micelles which can be formed from a single long rod are entropy favored.

Importance of the Research Problem

The possibilities of micellar systems and of other organized molecular assemblies (vesicles, microemulsions, lamellae, liposomes, etc.) were recognized many years ago and have been exploited in most of chemical applications with a view to improving or proposing new methodologies. This is currently a research area in constant development.[280-282]

Micelles possess many unique and advantageous properties. They have been shown to : (i) solubilize, concentrate, and organize solutes/ reactants; (ii) alter effective microenvironments (i.e., viscosity, polarity, acidity) about solubilized species; (iii) alter spectral parameters and quantum efficiencies of solubilizates; (iv) alter chemical and photochemical pathways and rates ; (v) be chemically stable, optically transparent, and relatively nontoxic.These micellar properties have been successfully employed to enhance a variety of analytical techniques including micellar enhanced chemiluminescence and chromatography.

The capability of aqueous surfactant aggregates to incorporate solutes is the reason for the widespread use of such systems in industrial, pharmaceutical, and synthetic chemical / catalytic applications.

Rates of many reactions have been shown to be accelerated by many orders of magnitude by carrying out reactions in appropriate aggregates. Among others, a relevant field of application is that of remediation of water and soil.

Surfactants are used in wide variety of applications, ranging from fire - extinguishing media to mucolytic agent in preparations for treating pulmonary diseases, and for cleaning contact lenses.[283,284] Most interestingly, they have attracted much attention in biological and medical research, especially in the efforts to develop new substitutes for blood.[285] To this end, a seemingly promising class of systems are microemulsions consisting of water, surfactant, and oil. Due to high solubility of oxygen in the latter, it is possible to keep animals alive even if their blood is substituted entirely by such systems.[286]

Cloud point is an important property of surfactants and is used in applications such as detergency since (i) adsorption of surfactants on substrates has been found to increase significantly near their cloud points,[287] and (ii) oily soil removal from substrates is optimized at the cloud point.[288] It is, therefore, advisable to operate in the vicinity of the cloud point for such applications.

The practical importance of CP lies in the fact that suspensions,[289] emulsions,[290] and ointments, stabilized with nonionic surfactants become unstable when heated in the vicinity of the CP, e.g., during steam sterilization, or some end uses. On the other hand, the rate of solubilization by surfactant solutions increases near their CP.[291] Foam control in many industrial processes is an important task because foaming can limit rate of these processes and usability of the products. It has been found that the foam stability drops at a temperature near the CP.[292]

The use of micellar solutions in different areas of analytical chemistry has attracted much attention in recent years and separations based on cloud point extractions are becoming an important and practical application in the use of surfactants in analytical chemistry.[293-295]

Surfactants are not present just by themselves, and other ingredients such as electrolytes, etc., commonly present in surfactant products, strongly affect their clouding behavior.[296] It is, therefore, important to understand the magnitude and nature of these additive effects as well as the mechanism involved, so that systems can be suitably tailored to exhibit clouding behavior at desired temperatures.

Due to reasons mentioned above and many more, the effect of additives on the clouding behavior of nonionic surfactants has been a subject of intense research. This thesis is devoted to study the effect of various classes of additives on the clouding behavior of an ionic surfactant, SDS.

Viscoelastic systems have a very high viscosity which might be of importance in enhanced performance and customer appeal of surfactant formulations. One of the fascinating aspect of these systems is the fact that slight change in the system on a microscopic level can lead to dramatic changes in the macroscopic properties of the system. Apart from the fact that these systems can be used as thickening agents, they are of practical interest for the preparation of emulsions and dispersions because they rule out any sedimentation. Keeping this in view, studies were also made on CTAB in presence of acids/salts for searching new viscoelastic systems.

Layout of the Thesis

This thesis consists of five chapters including this one. This chapter is concerned mainly with the general introduction of surfactants; the factors responsible for the formation of various aggregation patterns, their solution properties, e.g., solubilization, cloud point phenomenon,

viscoelasticity etc. An up-to-date literature survey related to the topic is also included. From the survey it appears that with non-ionic surfactants appearance of cloud point is an established fact but with ionic surfactants the situation is not the same and, very few reports are available on CP phenomenon in ionic systems.

Chapter-II includes methodologies which were used; the list of chemicals used; their formulae; make and % purity.

In ionic surfactants CP appears in the presence of high concentration of electrolytes. Chapter-III describes the study of cloud point phenomenon in SDS micellar systems in presence of different quaternary salts. Data of viscosity measurements on few systems in order to have an idea about the micellar shape/size as the system approaches CP are also included.

Cloud point of a system can be tuned with the aid of additives. Effect of various electrolytes and non-electrolytes on a chosen system is presented in Chapter-IV.

Keeping in view the importance of viscoelasticity, studies were made on CTAB micellar solutions in presence of sodium anthranilate : this is described in Chapter-V.

Chapter - II

Experimental

The chemicals used throughout the study are listed in Table 2.1 which also includes their abbreviated names, chemical formulas, sources, and purities.

All the surfactants (SDS, CTAB and Triton X-100) were used as received.

The quaternary salts were dried for at least 72 h before use in a vacuum drying oven. The temperature during drying was maintained according to the thermal stability and fusion point of the salt. The dried salts were stored over P_2O_5. Other inorganic salts were used as received.

All the organics (amines, alcohols, oils, amides, solvents, etc.) were used as supplied.

The water used to prepare the solutions was demineralized and double-distilled in an all-glass (Pyrex) distillation apparatus. The specific conductivity of the water was in the range 1-2 x 10^{-6} S cm^{-1}.

For the ^1H nuclear magnetic resonance (NMR) experiments, D_2O of 99.9% purity was supplied by the Heavy Water Division of BARC (Mumbai, India).

Special care was taken while cleaning the glassware (by immersing successively in 1 M NaOH-ethanol and 1 M nitric acid baths and then by rinsing with double-distilled water).

Stock solutions of surfactants (in water containing either a fixed concentration of salt or no salt) were prepared by weight.

SDS and quaternary salts were mainly used to observe the cloud point phenomenon. For the purpose different fixed concentrations of SDS were used with varying concentrations of quaternary salts.

To see the additive effect on CP, sample solutions were made by taking requisite amounts or volumes of additives (depending on their physical state) in standard volumetric flasks and making up the volumes with the stock solution. When required, more samples were prepared by dilution. After proper mixing, the sample solutions were kept overnight for equilibration. To avoid evaporation, the containers were kept properly stoppered during equilibration and measurement.

CP Measurements

CP's were obtained by placing several tubes, each containing a different [SDS] with fixed [salt], into a temperature controlled bath (designed and assembled in the laboratory with commercially available components). The temperature was ramped at the rate of 0.1 °C/min near the CP. Onset of turbidity (visual observation) was taken as the CP. However, the temperature was oscillated slowly through the CP until it was reproducible. Similar CP measurements were made by using different [salts] at fixed [SDS]. This was done by diluting the sample to smaller concentrations and by repeating the same procedure. These experiments were performed to obtain the minimum [salts] required to observe the clouding phenomenon for a fixed [SDS]. Few CP measurements were also performed with TX-100 + quaternary bromides by following the same procedure.

The system chosen to see the effect of various additives was 0.3M SDS + 0.25M Bu_4NBr (CP = 39.5 °C) as it provides a wider window for CP variation below and above the CP of the system.

Conductivity Measurements

A Philips conductivity meter (model 9500) equipped with platinized electrodes (cell constant: 1.02 cm^{-1}) was used for conductivity measurements.

For a typical measurement the sample solution was taken in a Pyrex glass container, the conductivity cell was introduced into it, which was then allowed to attain thermal equilibrium at the desired temperature. The conductivity was then noted. Temperature of the thermostat was raised to desired values and the conductivities were again noted. The solvent correction was made by deducting the conductivity of water from that of the sample solution.

Viscometry

All fluids may be considered to be consisting of molecular layers arranged one over the other. When a shearing force is applied to a liquid, it flows. However, the forces of friction between the layers offer resistance to this flow. Viscosity of a liquid is a measure of its frictional resistance. Viscosity is expressed as dyne-seconds per cm^2 or poise. In practice, smaller units centipoise and millipoise are used.

Viscosity of a liquid can be determined with the help of Poiseulle's equation which governs the flow of a liquid through a capillary. If *l* is the length of the capillary, r its radius, p the pressure difference at the ends, then the volume flowing per second through the capillary, then η the coefficient of viscosity is given by

$$\eta = \pi r^4 pt / 8 lv \qquad (2.1)$$

It is not possible to find the absolute coefficient of viscosity (η) straight away from Poiseulle's equation as experimental measurement of p, r, l and v offers considerable difficulty.

Hence viscosity of a liquid is determined with respect to another liquid, usually water. This is called relative viscosity.

Let t_1 and t_2 be the times of flow of a fixed volume V of the two liquids through the same capillary. The expression for relative viscosity (η_r) can be derived from eq. (2.3)

$$\eta_r = \frac{\eta_1}{\eta_2} = \frac{\pi p_1 r^4 t_1}{8\, l v} \cdot \frac{8\, l v}{\pi p_2 r^4 t_2} = \frac{p_1 t_1}{p_2 t_2} \qquad (2.2)$$

Since the pressure is proportional to the density, we have

$$\eta_r = \frac{d_1 t_1}{d_2 t_2} \qquad (2.3)$$

where d_1 and d_2 are the densities of the solution and solvent. Ozeki and Ikeda[297] found density corrections to be negligible, η_r values may, therefore, be calculated using eq. (2.4)

$$\eta_r = \frac{t_1}{t_2} \qquad (2.4)$$

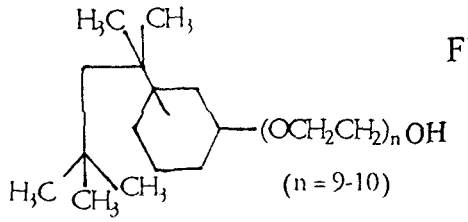
In the present study the viscosities of the solutions were measured at different temperatures upto just below the CP by an Ubbelohde viscometer thermostated at the experimental temperature. The temperature was controlled within ±0.1 °C in a thermostated water bath. The flow times always exceeded 150s, and no kinematic corrections were necessary.

^{1}H NMR Measurement

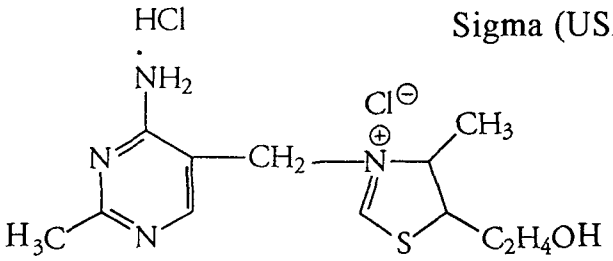
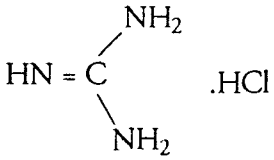
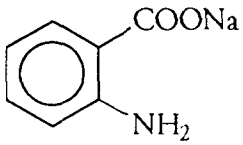
^{1}H NMR spectra were recorded in D_2O on a Bruker DPX-300 spectrometer (Karlsruhe, Germany) operating at 300 MHz in 5-mm thin-walled NMR tubes with the peak for D_2O as the internal standard.

^{1}H NMR spectra were run on aqueous solutions of 10 mM CTAB in the presence and absence of added sodium anthranilate.

Table 2.1: Names and Structural Formulas of the Chemicals Used.

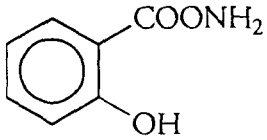
Name	Abbreviation	Structure/Formula	Make	% purity
a. Surfactants				
Sodium dodecyl sulfate	SDS	$C_{12}H_{25}OSO_3^- Na^+$	Fluka (Switzerland)	≥ 98
Cetyltrimethylammonium bromide	CTAB	$C_{16}H_{33}(CH_3)_3 N^+Br^-$	Merck (Germany)	99
Polyethylene glycol *tert*–octylphenyl ether	TX-100		Fluka (Switzerland)	(~99)
b. Salts				
Tetra *n*-butylammonium bromide	Bu_4NBr	$(n\text{-}C_4H_9)_4NBr$	Fluka (Switzerland)	> 98
Tetra *n*-amylammonium bromide	Am_4NBr	$(n\text{-}C_5H_{11})_4NBr$	Fluka (Switzerland)	≥ 99
Tetra *n*-butylphosphonium bromide	Bu_4PBr	$(n\text{-}C_4H_9)_4PBr$	Fluka (Switzerland)	≥ 98
Sodium nitrate		$NaNO_3$	Ranbaxy (India)	98
Sodium sulfate		Na_2SO_4	Qualigens (India)	98
Sodium orthophosphate		$Na_3PO_4.\ 12H_2O$	BDH (England)	

contd.....

Thiamine hydrochloride	T.HCl		Sigma (USA)	99
Guinidine hydrochloride	Gu.HCl		Riedel–de–Haen (Germany)	99
Sodium anthranilate	NaAn		CPC (USA)	98
c. Sugars				
D(+)–Glucose		$C_6H_{12}O_6$	E. Merck (India)	99
D(–)–Arabinose		$C_5H_{10}O_5$	Fluka (Switzerland)	≥ 99
D(+)–Xylose		$C_5H_{10}O_5$	Fluka (Switzerland)	≥ 99

contd.....

d. Amides

Formamide	$HCONH_2$	Fluka (Switzerland)	98.5
Acetamide	CH_3CONH_2	E. Merck (India)	99
N,N–Dimethylformamide	$HCON(CH_3)_2$	Merck (Germany)	99.5
Thioacetamide	CH_3CSNH_2	Merck (Germany)	98
Salicylamide		Merck (Germany)	
Urea	NH_2CONH_2	BDH (England)	99
Thiourea	NH_2CSNH_2	s.d. fine (India)	99
Tetramethylurea	$(CH_3)_2NCON(CH_3)_2$	Fluka (Switzerland)	99
Tetramethylthiourea	$(CH_3)_2$ $NCSN(CH_3)_2$	TCI (Japan)	99

e. Amines

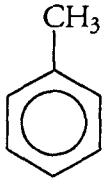
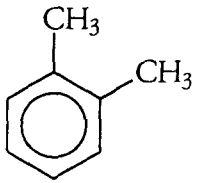
n–Hexylamine	C_6NH_2	$CH_3(CH_2)_5NH_2$	Merck (Germany)	98
n–Heptylamine	C_7NH_2	$CH_3(CH_2)_6NH_2$	Fluka (Switzerland)	> 98
n–Octylamine	C_8NH_2	$CH_3(CH_2)_7NH_2$	Fluka (Switzerland)	> 98

contd.....

f. Alcohols

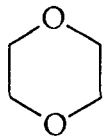
n–Hexanol	C_6OH	$CH_3(CH_2)_5OH$	BDH (England)	99
n–Heptanol	C_7OH	$CH_3(CH_2)_6OH$	BDH (Englnd)	99
n–Octanol	C_8OH	$CH_3(CH_2)_7OH$	Fluka (Switzerland)	97

g. Aliphatic/Aromatic Oils

n–Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	E. Merck (India)	98
n–Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	Qualigens (India)	99
Benzene	C_6H_6		E. Merck (India)	99
Toluene	$C_6H_5CH_3$		s.d. fine (India)	99
o-Xylene	C_8H_{10}		E. Merck (India)	99.9

contd.....

h. Organic solvents

Dioxane			Ranbaxy (India)	99.8
Dimethyl sulfoxide	DMSO	CH_3SOCH_3	SRL (India)	99.8
Ethylene glycol		$CH_2(OH)CH_2OH$	BDH (England)	95
Propylene glycol		$CH_3CH(OH)CH_2OH$	BDH (England)	95

i. Acids

Malic acid		$HOOCCH(OH)CH_2COOH$	s.d. fine (India)	99
Thiomalic acid		$HOOCCH\ (SH)\ CH_2COOH$	Fluka (Switzerland)	> 99

Chapter - III

Clouding Phenomenon in Sodium Dodecyl Sulfate + Quaternary Bromide Systems

Introduction

Aqueous solutions of nonionic surfactants are well known for their propensity to undergo clouding[241,297,298] on heating followed by formation of two coexisting isotropic phases. Certain zwitterionic surfactants[299], as well as some ionic surfactants in presence of high concentrations of added salt[242], also exhibit such phase separations. However, the mechanism via which the phenomenon occurs remains obscure. It has been reported that the increase of hydrophobic character near the headgroup region (going from tri-*n*-propyl to tri-*n*-butyl) in a cationic surfactant has shown a departure of the behavior of producing stable solutions at elevated tempertures.[243] Though the microscopic origin is far to settle, Hayter and Zulauf[241] have explained the origin of cloud point phenomenon in nonionic surfactant systems. They suggested that the phase separation in micellar solution is due to the van der Waals attractive energy between the micelles, and there exists a barrier between the micelles which is brought about by the presence of at least a monolayer of highly structured water at each micellar surface, which is weakened with increasing temperature.

In the ionic surfactant systems the situation is more complex. Since the micelles are charged, there must be an electrostatic repulsion between the micelles in addition to the van der Waals attraction force. If one considers these two forces alone, the cloud point would be decreased on adding the electrolyte, since the electrical repulsion force is weakened by the electrolyte. It has been observed that the cloud point is changed in just the opposite direction. Moreover, in the systems of equimolar mixture of anionic and cationic surfactants, the micelles are essentially neutral, giving a very much lower electrical repulsion force between the micelles;[300] yet, in this case no cloud point phenomenon was observed.

This strongly suggests that the change of electrical repulsion force is not very important for the occurrence of the cloud point phenomenon and there must be other forces between the micelles besides these two forces. Mikulich[301] reported that the degree of solvation increases with increasing headgroup size. The solvation which is a universal phenomenon for all ionic micellar systems is a factor acting against the occurrence of the cloud point phenomenon.

It is well established that the addition of ionic surfactants increases the cloud points of their nonionic counterparts[302,303] and the increase depends on composition of the mixed micelle. Valaulikar and Manohar[304] have demonstrated that the increase in cloud point can be described in terms of the surface charge per nicelle which is responsible for electrostatic repulsion between the micelles. This supports the view point that micelle coalescence, rather than micellar growth, is responsible for the clouding process. Hence, if the introduction of charge delays the phase separation, depletion of the charge on an ionic micelle could cause resumption of the phenomenon. Thus, charge could be one of the factors to tune the CP, especially in ionic micellar solutions.

The above facts show that not only the heating but also other equally important factors are responsible for CP phenomenon. It is, therefore, desirable to have systems suitably tailored to exhibit clouding behavior at the application temperature. There are few intelligent models available for the nonionic surfactants, which give quantitative footing to the CP data.[305-307] For the ionic surfactants no such generalization is available. In view of the increasing utilization of phase behavior of the ionic surfactant solutions for a variety of applications, including an alternative approach for extractive preconcentration in chemical analysis,[9,308,309] this is timely to have a quantitative generalization with ionic surfactants too.

With the above view point systematic investigations on the CP phenomenon in an anionic surfactant (SDS) with different quaternary bromide salts (Bu_4NBr, Am_4NBr and Bu_4PBr) were performed.

CP-measurements were also made with TX-100 in presence of the quaternary bromides for comparison purpose. A few viscosity measurements were performed in SDS+quaternary salt systems to have a rough idea about micellar size as individual systems approach the CP. Conductivities of pure SDS (0.3M), pure Bu_4NBr (0.2M) and a mixture of SDS (0.3M) and Bu_4NBr (0.2M) were also measured with temperature to see whether or not the substitution of Na^+ by Bu_4N^+ from the micellar surface is taking place.

The purpose of the study is multifold : (i) to study clouding phenomenon in anionic SDS surfactant; (ii) to establish [SDS]/[salt] ratios for the appearance of clouding; (iii) to compare the behavior of TX-100 in order to see the effect of hydration states of the two kinds of micellar interfaces; (iv) to see the role of [salt]–temperature compensation in observing the CP.

Results

The CP values of SDS+quaternary bromide salt systems are collected in Tables 3.1 – 3.4. The data for variation of conductivity with temperature for pure SDS, pure Bu_4NBr and SDS + Bu_4NBr mixture are given in Table 3.5. The relative viscosities of SDS micellar solutions with different quaternary salts at different temperatures (upto just below the CP) are given in Tables 3.6 - 3.8. CP values for TX-100 + quaternary bromide systems are collected in Table 3.9. Tables 3.10–3.12 record the concentrations of SDS and quaternary salts required for CP appearance at

different temperatures. Linear regression data for plots of [salt] needed per mole of surfactant with temperature are complied in Table 3.13.

Figs. 3.1–3.3 show the variation of CP of SDS solutions with added salt concentrations whereas the CP data observed with various combinations of Bu_4NBr and SDS concentrations are depicted in Fig. 3.4. Fig. 3.5 illustrates the variation of conductivity of SDS, Bu_4NBr, and SDS + Bu_4NBr systems with temperature. η_r variations with different salts are depicted in Figs. 3.6-3.8. Fig. 3.9 illustrates the CP behavior of TX-100 in presence of the three quaternary salts. Figs. 3.10-3.12 show the plots of concentrations of SDS and quaternary salts required for CP appearance at different temperatures. Fig. 3.13 shows the variation of the amounts of salts per mole of SDS (i.e. slope, S) needed for getting CP with temperature.

Discussion

We can see from Figs. 3.1-3.3 that with each SDS solution there is a need of certain minimum [salt] before the system could show clouding (~95 °C). From perusal of the data it is also clear that CP decreases with the increase of salt concentration while an increase is observed with increase in surfactant concentration (Fig. 3.4). Further, an increase in alkyl part of the quaternary salt produces the phenomenon at lower salt concentrations (Fig. 3.2), whereas replacement of N with P-atom in the quaternary salt shifts the occurrence of CP-phenomenon to lower [salt] (Fig. 3.3).

In earlier studies[310-312] it has been proposed that in SDS-organic additive systems the alkyl chains could penetrate into the micelle with polar groups remaining in the head group region. In a separate SANS

Table 3.1: Cloud Point (^{0}C) data on XmM SDS + YmM Bu_4NBr systems.

	X=10	50	100	200	300
Y	CP	CP	CP	CP	CP
400 0	23 1	23 0	24 5	26 0	28 0
350 0	23 3	23 2	25 4	28 5	30 0
325 0	23 8	23 6	25 8	29 0	32 0
300 0	24 4	23 8	24 8	30 3	34 2
250 0	25 0	24 9	26 3	33 8	39 0
200 0	26 0	26 4	30 0	39 0	57 0
190 0	26 2	26 4	31 0	40 0	68 0
185 0	26 3	26 9	31 9	41 0	73 0
180 0	26 4	27 0	32 5	44 0	78 0
175 0	26 5	27 3	33 0	46 0	85 0
170 0	26 5	27 5	33 5	53 6	98 0
165 0	26 9	28 0	34 0	60 0	
160 0				64 0	
155 0				68 0	
150 0	27 2	28 5	35 0	72 0	
145 0				77 0	
140 0				81 0	
135 0				98 0	
130 0					
100 0	29 3	32 8	44 0		
85 0			49 0		
75 0		36 0	56 0		
65 0	31 0	40 0	65 0		
60 0			81 0		
57 5			98 0		
50 0	32 9	50 0			
40 0	35 0	62 0			
35 0		80 0			
32 5		95 0			
30 0	37 1				
20 0	41 5				
10 0	58 0				
7 5	73 1				
6 5	80 0				
6 0	89 0				
5 7	96 0				
5 5					

Table 3.2: Cloud Point (^{0}C) data on XmM SDS + YmM Am_4NBr systems.

X = 10		50		100		200		300	
Y	CP	Y	CP	Y	CP	Y	CP	Y	CP
2 76	41 5	19 35	43 1	33 33	53 5	60 00	39 3	88 23	42 3
2 73	43 5	19 20	44 7	32 23	56 2	59 02	43 0	86 96	47 3
2 66	45 5	19 05	46 2	31 68	58 0	58 06	47 8	86 21	50 1
2 56	47 5	18 89	47 8	31 06	61 5	57 14	52 3	85 47	53 5
2 47	49 5	18 75	49 5	30 47	64 0	56 25	56 5	84 75	57 0
2 39	51 5	18 60	51 0	29 90	67 0	55 38	64 3	84 03	60 7
2 30	53 4	18 46	53 0	29 36	70 0	54 54	69 0	83 33	64 8
2 23	55 9	18 32	54 6	28 83	73 5	53 73	75 5	82 64	69 5
2 17	58 5	18 18	55 9	28 32	77 5	52 94	79 5	81 96	73 0
2 06	62 5	18 45	57 5	27 35	81 0	52 17	85 0	80 86	79 0
1 97	64 5	17 77	60 5	27 83	85 0	51 43	94 5	79 78	84 5
1 80	67 5	17 52	64 0	27 35	90 0			78 95	90 0
1 66	70 5	17 26	66 5	27 16	92 0			78 12	98 0
1 52	73 0	17 02	70 0	26 98	94 0				
1 35	78 0	16 78	73 0	26 8	96 5				
1 22	80 5	16 55	76 5						
1 07	84 0	16 32	79 5						
0 95	86 5	16 11	83 5						
0 86	88 5	15 89	86 5						
0 78	90 0	15 68	90 0						
0 72	91 0	15 60	91 5						
0 66	92 5	15 52	93 0						
0 61	93 5	15 44	94 5						
		15 36	95 5						

Table 3.3: Cloud Point (^{0}C) data on XmM SDS + YmM Bu_4PBr systems.

X = 10		50		100		200		300	
Y	CP	Y	CP	Y	CP	Y	CP	Y	CP
10 0	28 5	50 0	21 5	100 0	21 0	171 4	22 5	250 0	22 0
9 4	30 2	46 9	23 5	90 9	22 0	157 9	26 0	214 3	27 5
8 6	32 8	42 9	26 5	83 3	25 5	146 3	29 5	197 4	35 5
8 1	35 4	39 5	30 0	76 9	28 8	136 4	33 5	182 9	40 5
7 7	37 2	36 5	34 0	71 4	34 5	127 7	42 5	170 5	51 5
7 3	39 6	34 1	38 7	69 9	38 0	122 5	50 0	159 6	61 0
7 0	42 8	31 9	44 9	66 7	41 2	120 0	53 0	153 1	61 5
6 7	45 5	30 6	49 9	64 5	44 8	117 6	57 5	150 0	66 5
6 4	49 0	29 4	55 5	62 5	49 0	115 4	62 5	147 1	73 5
6 1	52 4	28 3	62 0	60 0	53 1	113 2	67 0	144 2	84 0
5 9	55 7	27 3	68 5	58 8	58 3	111 1	73 0	142 9	85 5
5 7	60 0	26 3	75 5	57 1	63 5	109 1	80 5	141 5	89 0
5 5	63 5	25 4	82 5	56 3	67 5	108 1	84 5	140 2	93 5
5 3	67 5	24 6	88 5	55 6	70 0	107 1	87 0		
5 1	70 5	24 4	93 0	54 8	73 5	106 2	90 0		
4 9	73 5			54 1	77 0	105 3	94 0		
4 8	76 5			53 3	81 0				
4 6	79 0			52 6	84 5				
4 5	81 5			51 9	89 0				
4 3	84 5			51 3	93 5				
4 2	86 5			50 6	95 0				
4 1	89 5								
3 9	92 5								
3 7	95 5								

Table 3.4: Cloud Point (^{0}C) data on X mM SDS + YmM Bu_4NBr systems.

	Y=100	150	200	250	300
X	CP	CP	CP	CP	CP
10.0	29.3	27.2	26.0	25.0	24.4
50.0	33.8	29.0	26.4	24.9	23.8
75.0	38.6				
100.0	44.0	35.0	30.0	26.3	24.8
125.0	52.0	41.0			
150.0	66.0	47.0	36.0	29.0	27.3
175.0	71.0	56.0			
180.0	83.0				
182.5	96.0				
188.0					
200.0		72.0	39.0	33.8	30.3
225.0		81.0			
250.0		98.0	47.5	36.8	32.2
275.0					
300.0			57.0	39.5	34.2
325.0			63.0		
350.0			68.0	44.0	38.0
355.0			79.0		
365.0			94.0		
375.0				49.0	
400.0				56.0	45.0
410.0				63.0	
420.0				74.0	
430.0				83.0	
440.0				96.0	
450.0					60.0
500.0					74.0
510.0					82.0
520.0					88.0
530.0					96.0
540.0					

Table 3.5 : Variation of specific conductivity with temperature of 0.3 M SDS, 0.2 M Bu_4NBr, and 0.3 M SDS + 0.2 M Bu_4NBr systems.

Temp (^{0}C)	10^5 x Specific conductivity (Scm^{-1})		
	0.3 M SDS	0.2 M Bu_4NBr	0.3M SDS+ 0.2 M Bu_4NBr
25.0	0.89	1.04	1.85
30.0	0.98	1.13	1.96
35.0	1.14	1.23	2.14
40.0	1.25	1.36	2.35
45.0	1.39	1.49	2.60
47.5	1.44	1.55	2.65
50.0	1.50	1.63	2.76
51.0	1.53	1.67	2.80
52.0	1.56	1.69	2.85
53.0	1.59	1.72	2.89
54.0	1.63	1.75	2.93
55.5	1.68	1.80	2.97
56.0	1.70	1.84	3.01

Table 3.6 : Relative viscosity (η_r) data for 100 mM SDS + Y mM Bu_4NBr at different temperatures.

Temp.(°C)	η_r			
	Y=100	**150**	**200**	**250**
15.0	1.577	1.842	1.909	1.902
20.0	1.797	1.977	1.990	1.970
25.0	1.948	2.108	2.133	2.120
26.3				turbid
29.5			2.177	
30.0	2.048	2.150	turbid	
32.0		turbid		
35.0	2.090			
40.0	2.330			
41.8	turbid			

Table 3.7 : Relative viscosity (η_r) data for 100 mM SDS + quaternary bromides at different temperatures.

Temp.(°C)	η_r		
	[Bu_4NBr]=60mM	[Bu_4PBr]=73mM	[Am_4NBr]=30mM
25.0		3.96	1.65
28.0		3.94	
30.0	3.49	3.92	1.59
32.0		4.04	
34.0		4.23	
34.5		turbid	
35.0	3.36		1.52
40.0	3.25		1.44
45.0	3.08		1.39
48.0	2.97		
50.0			1.37
51.0	2.93		
51.5			1.38
53.0	2.94		1.42
53.8	turbid		
55.0			1.51
55.5			turbid

Table 3.8 : Relative viscosity (η_r) data for 300mM SDS + quaternary bromides

Temp.(°C)	η_r		
	[Bu_4NBr]=300mM	[Bu_4PBr]=182mM	[Am_4NBr]=94mM
25.0	2.005	3.116	4.985
30.0	1.964	2.925	4.427
34.0	1.990		
35.0	turbid	2.839	4.315
39.0			4.138
40.0		2.673	turbid
40.5		2.670	
41.0		turbid	

Table 3.9 : Cloud Point (^{0}C) data for 50 mM TX-100 + quaternary salt systems as a function of salt concentrations.

[Bu_4NBr](mM)	CP	[Bu_4PBr](mM)	CP	[Am_4NBr](mM)	CP
23.8	70.0	3.6	70.0	1.1	70.5
45.5	74.5	4.3	71.0	1.3	71.5
65.2	78.0	5.2	72.0	1.4	72.5
83.3	81.5	6.6	73.0	1.8	74.0
100.0	84.5	8.3	75.0	2.2	76.5
115.0	87.5	9.6	76.0	2.8	79.0
129.6	90.5	10.9	77.5	3.4	81.0
		16.6	80.5	4.1	82.0
		31.3	85.0	4.9	83.0
		45.0	89.0	5.8	84.5
		58.8	93.0	7.2	87.5
				8.6	89.0
				10.0	90.5
				10.9	91.0

Table 3.10 : Values of the concentrations of SDS (XmM) and Bu_4NBr (YmM) required for CP appearance at the indicated temperatures.

	CP=30°C	50°C	70°C	95°C
X	Y	Y	Y	Y
10.0	70.0	12.5	7.5	5.8
50.0	125.0	50.0	37.0	32.5
100.0	200.0	82.0	63.5	57.5
182.0				100.0
200.0	300.0	172.5	150.0	135.0
250.0				150.0
300.0	350.0	212.5	182.5	170.0

Table 3.11 : Values of the concentrations of SDS (XmM) and Am_4NBr (YmM) required for CP appearance at the indicated temperatures.

	CP=50°C	70°C	95°C
X	Y	Y	Y
10.0	2.47	1.67	0.61
50.0	18.75	17.20	15.36
100.0	33.60	29.90	26.80
200.0	57.50	54.54	51.43
300.0	86.21	82.64	78.12

Table 3.12 : Values of the concentrations of SDS (XmM) and Bu_4PBr (YmM) required for CP appearance at the indicated temperatures.

	CP=30^0	50^{0}C	70^{0}C	95^{0}C
X	Y	Y	Y	Y
10.0	9.37	6.20	5.08	3.70
25.0	23.43	16.66	14.50	12.71
50.0	39.47	30.61	27.00	24.39
75.0	56.60	45.00	47.95	
100.0	75.50	62.00	55.55	51.50
200.0	146.34	122.45	112.00	105.26
300.0	192.00	159.70	147.50	140.18

Table 3.13 : Linear Regression data (slopes, S; intercepts, I, and regression coefficients, r) for the plots illustrated in Figures 3.10-3.12.

Temp.	Bu_4NBr			Bu_4PBr			Am_4NBr		
(°C)	S	I(mM)	r	S	I(mM)	r	S	I(mM)	r
30.0	0.973	80.497	0.981	0.639	8.145	0.996			
50.0	0.706	12.679	0.990	0.541	4.428	0.995	0.279	2.877	0.997
70.0	0.628	5.114	0.988	0.502	2.987	0.996	0.271	1.448	0.998
95.0	0.583	1.895	0.991	0.481	1.382	0.996	0.260	0.132	0.998

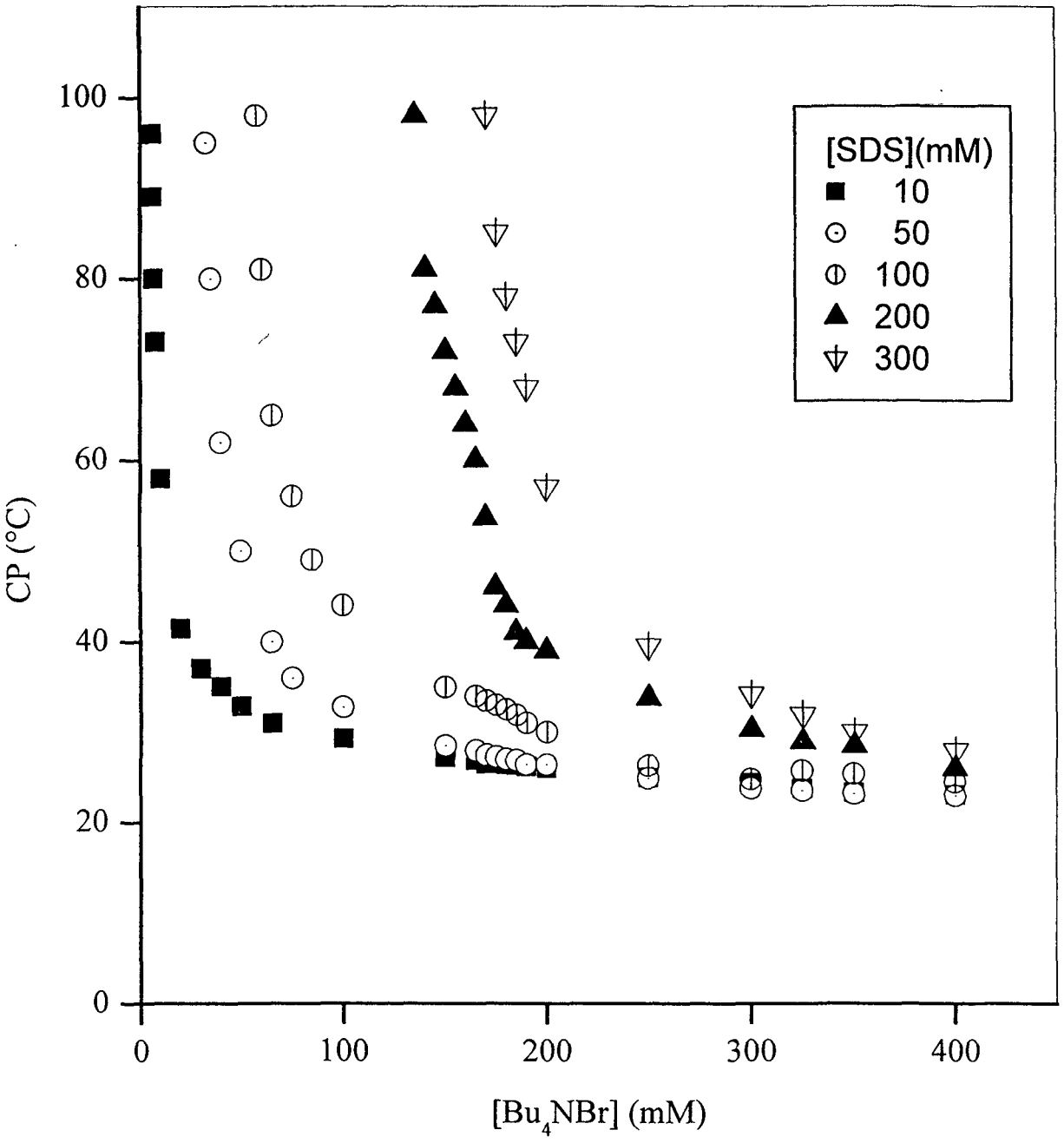


Fig. 3.1 : Variation of Cloud Point with [Bu_4NBr] at different fixed [SDS]

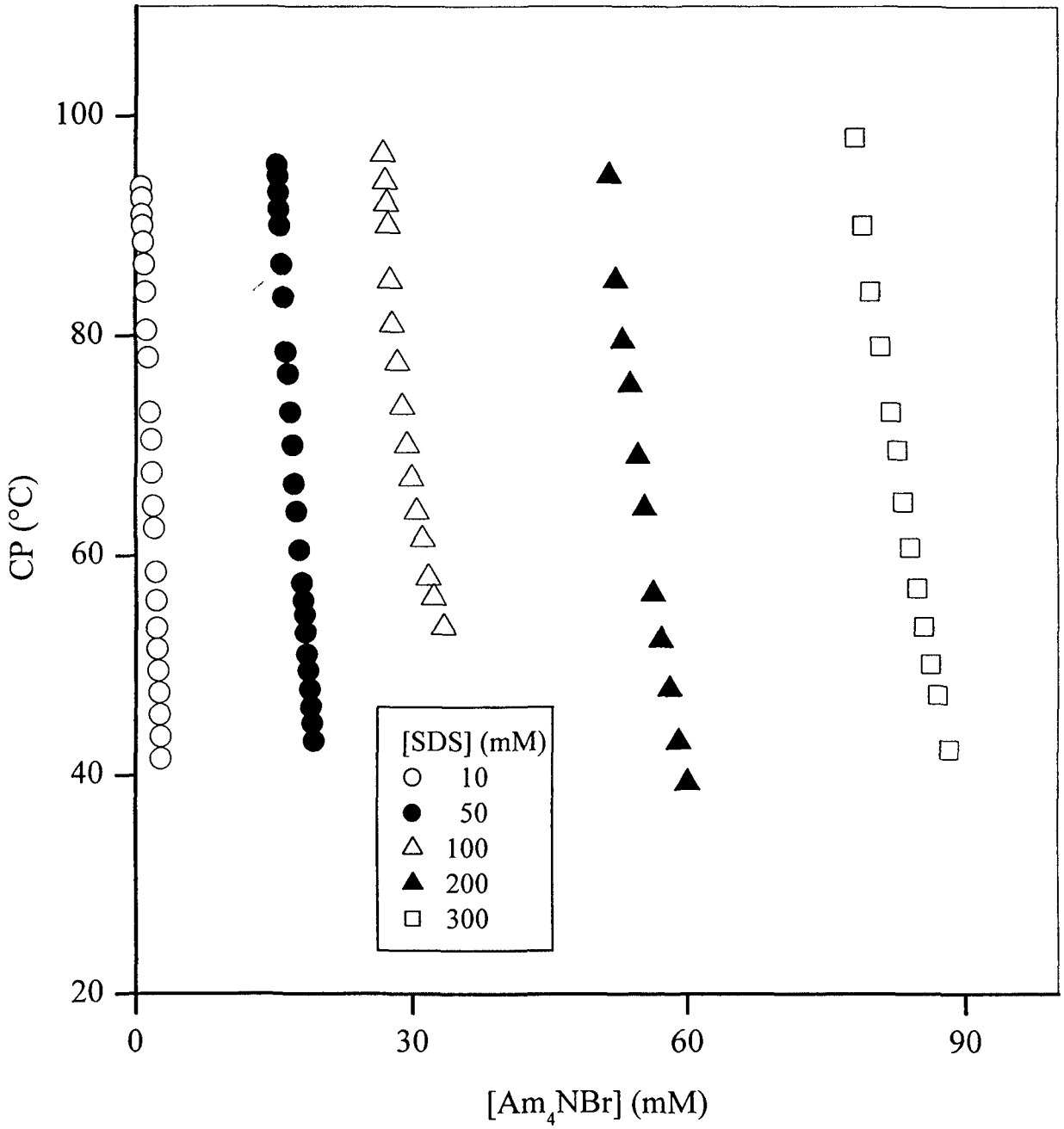


Fig. 3.2 : Variation of Cloud Point with [Am_4NBr] at different fixed [SDS].

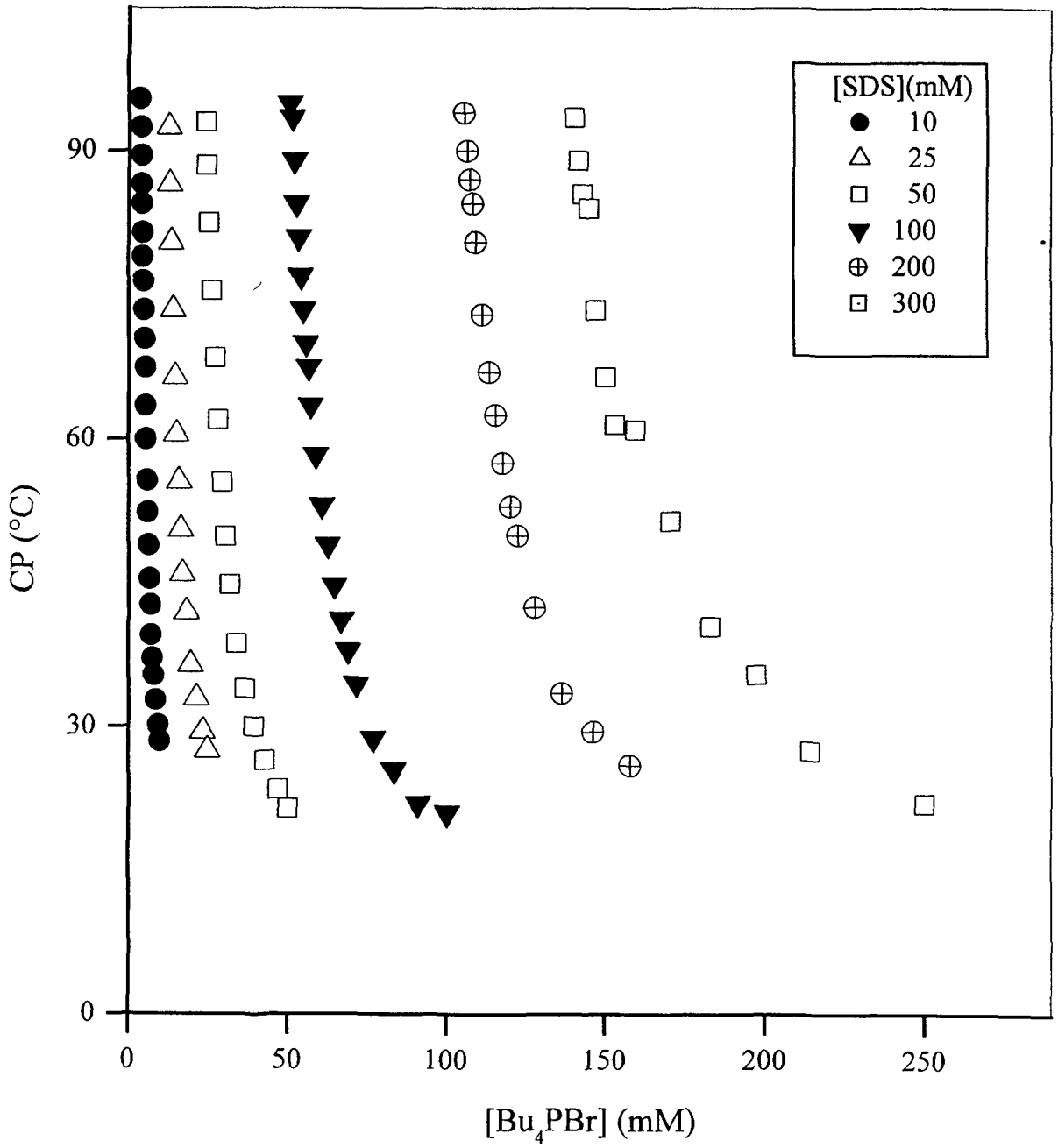


Fig. 3.3 : Variation of Cloud Point with [Bu_4PBr] at different fixed [SDS].

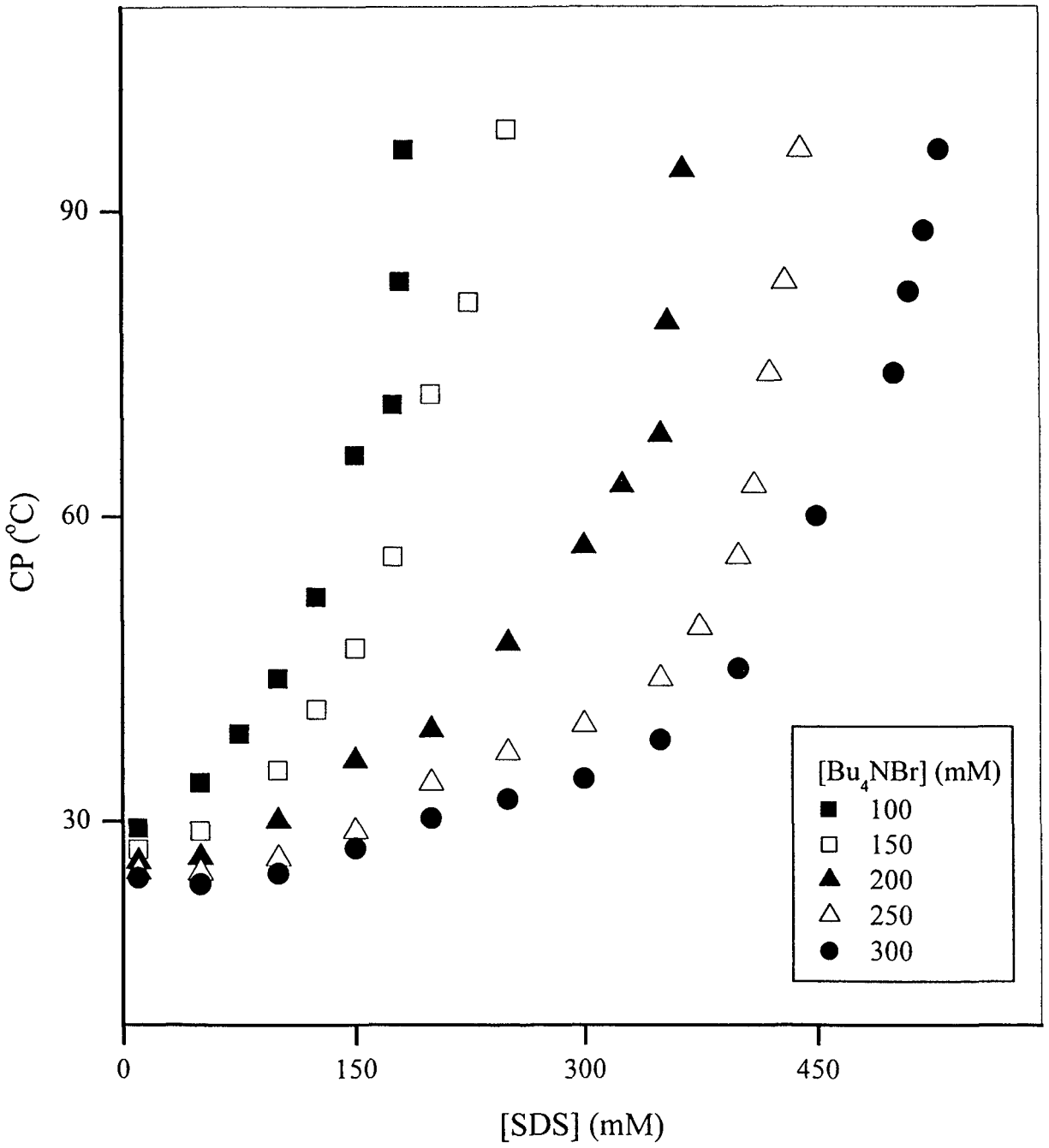


Fig. 3.4 : Variation of Cloud Point with [SDS] at different fixed [Bu_4NBr].

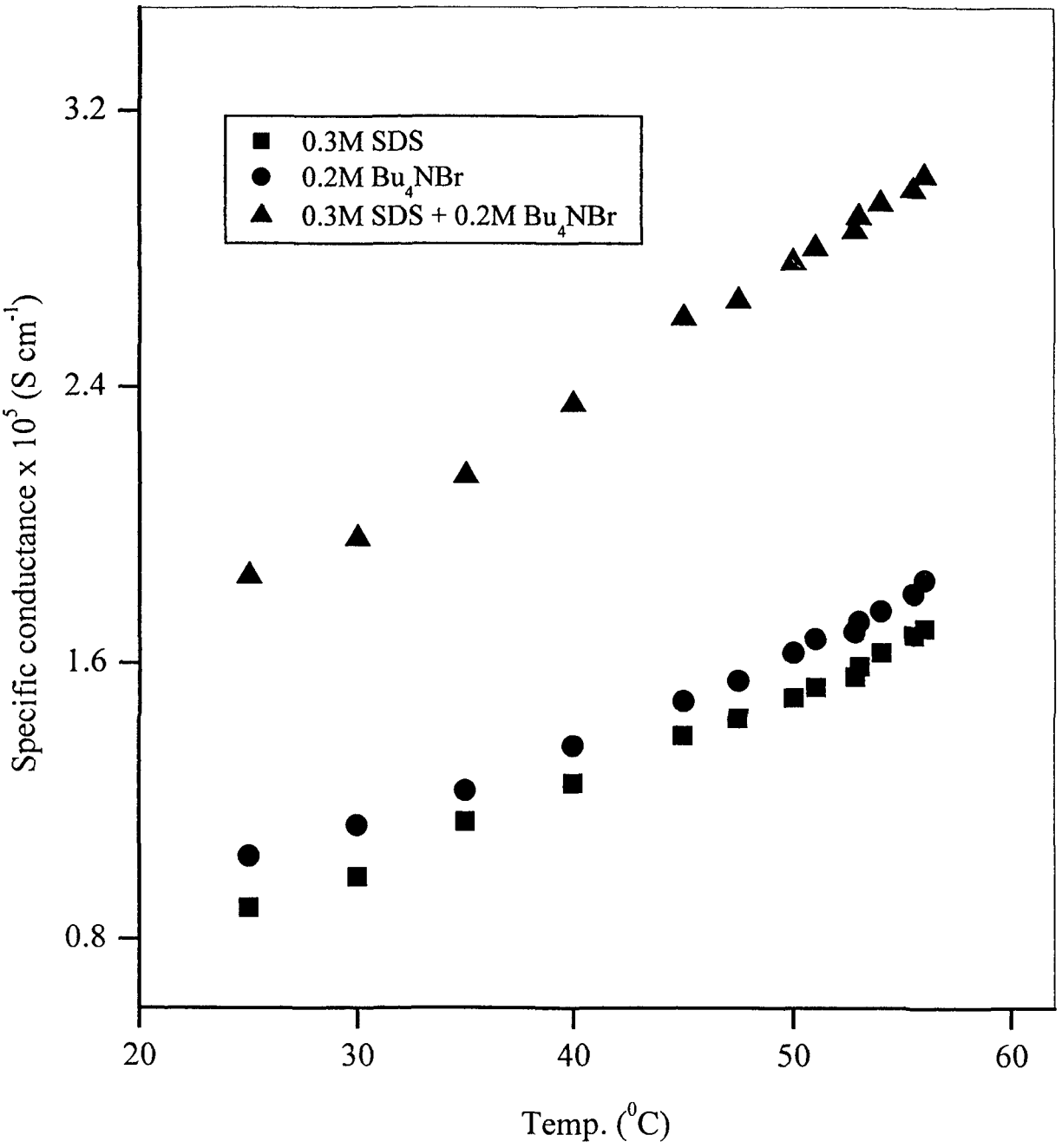


Fig. 3.5 : Variation of specific conductivity with temperature.

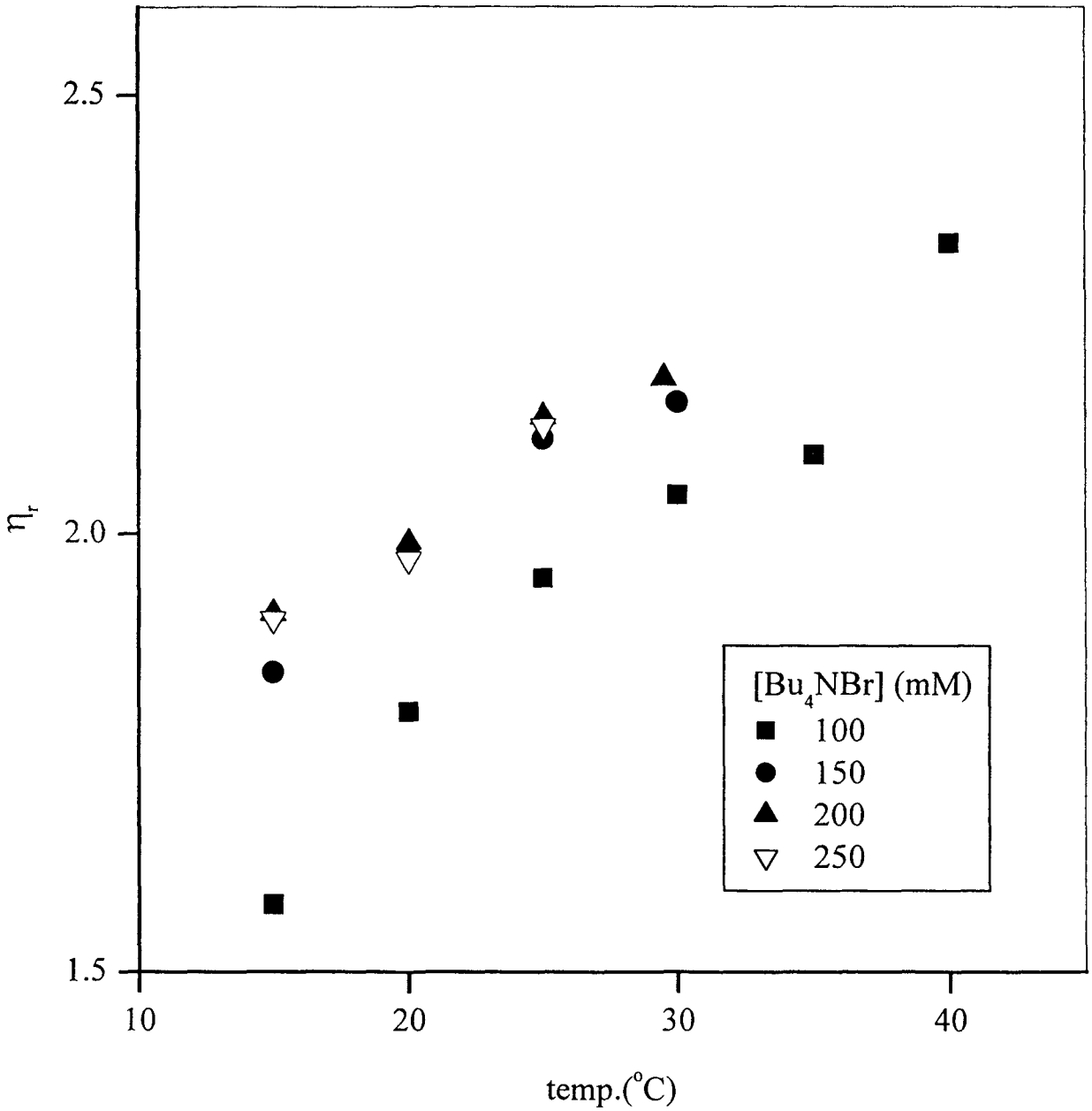


Fig. 3.6 : Variation of relative viscosity of 100 mM SDS + Bu_4NBr systems with temperatures.

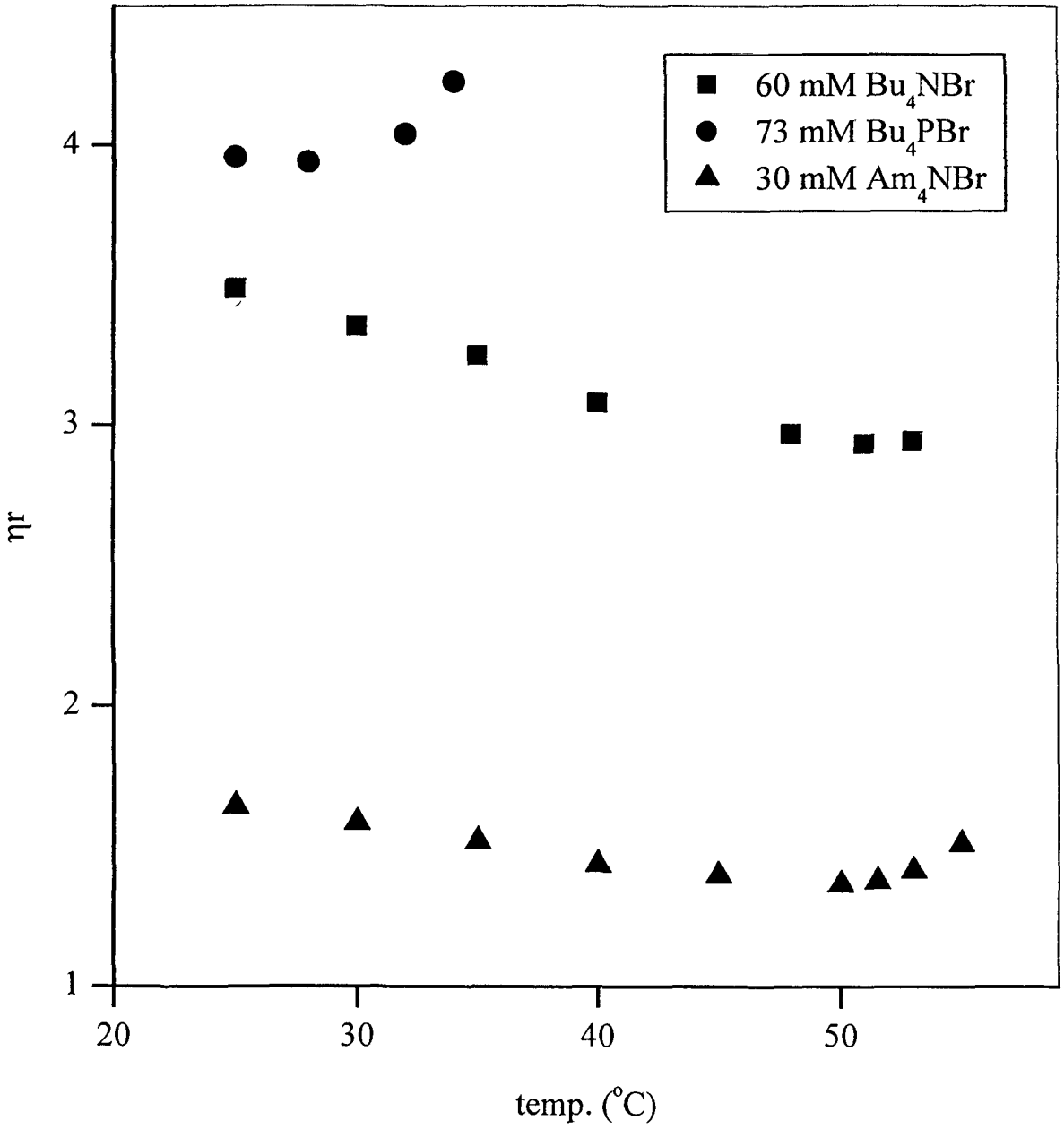


Fig. 3.7 : Variation of relative viscosity of 100 mM SDS + salt systems with temperature.

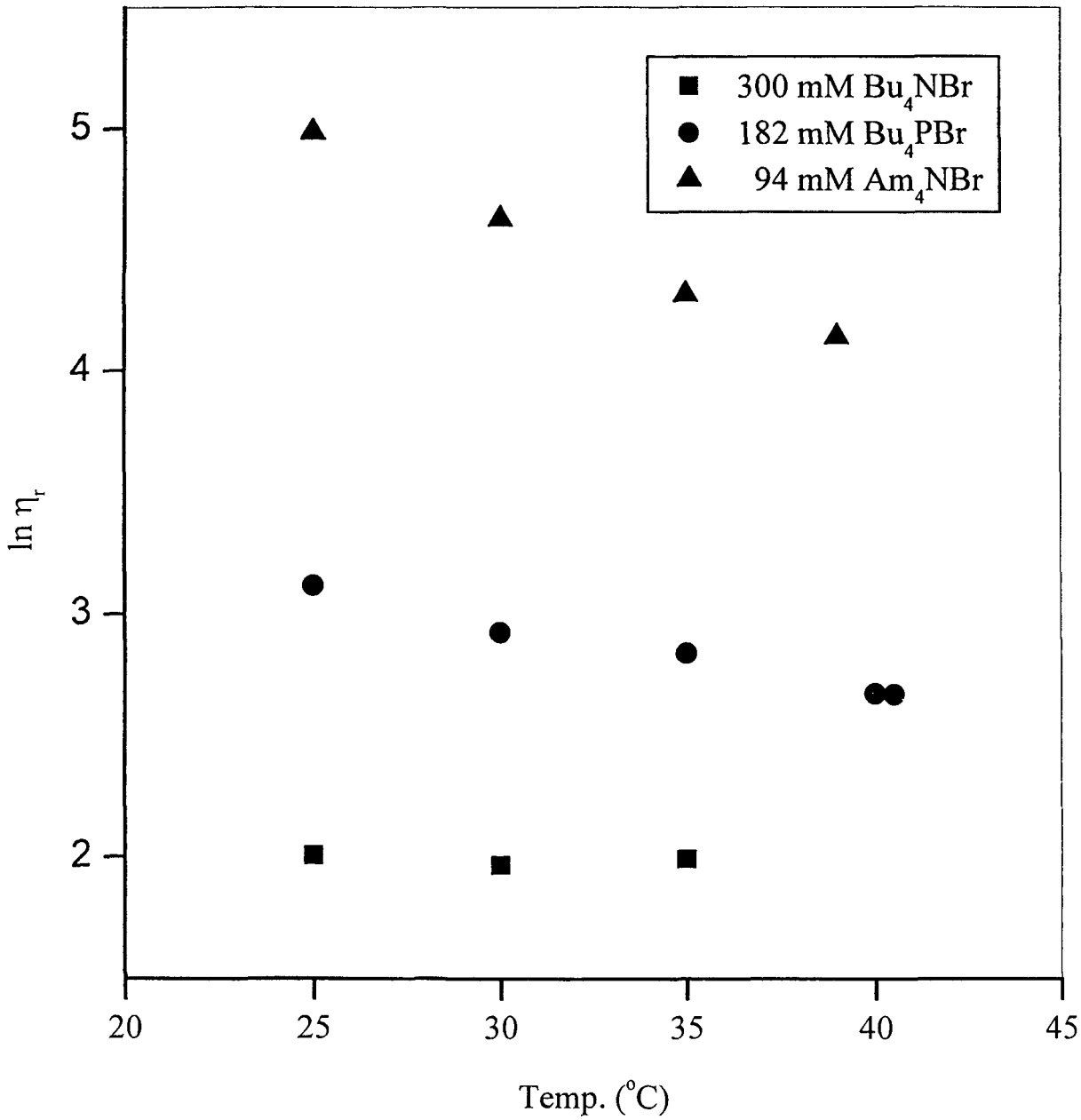


Fig. 3.8 : Variation of relative viscosity of 300 mM SDS + salt systems with temperature.

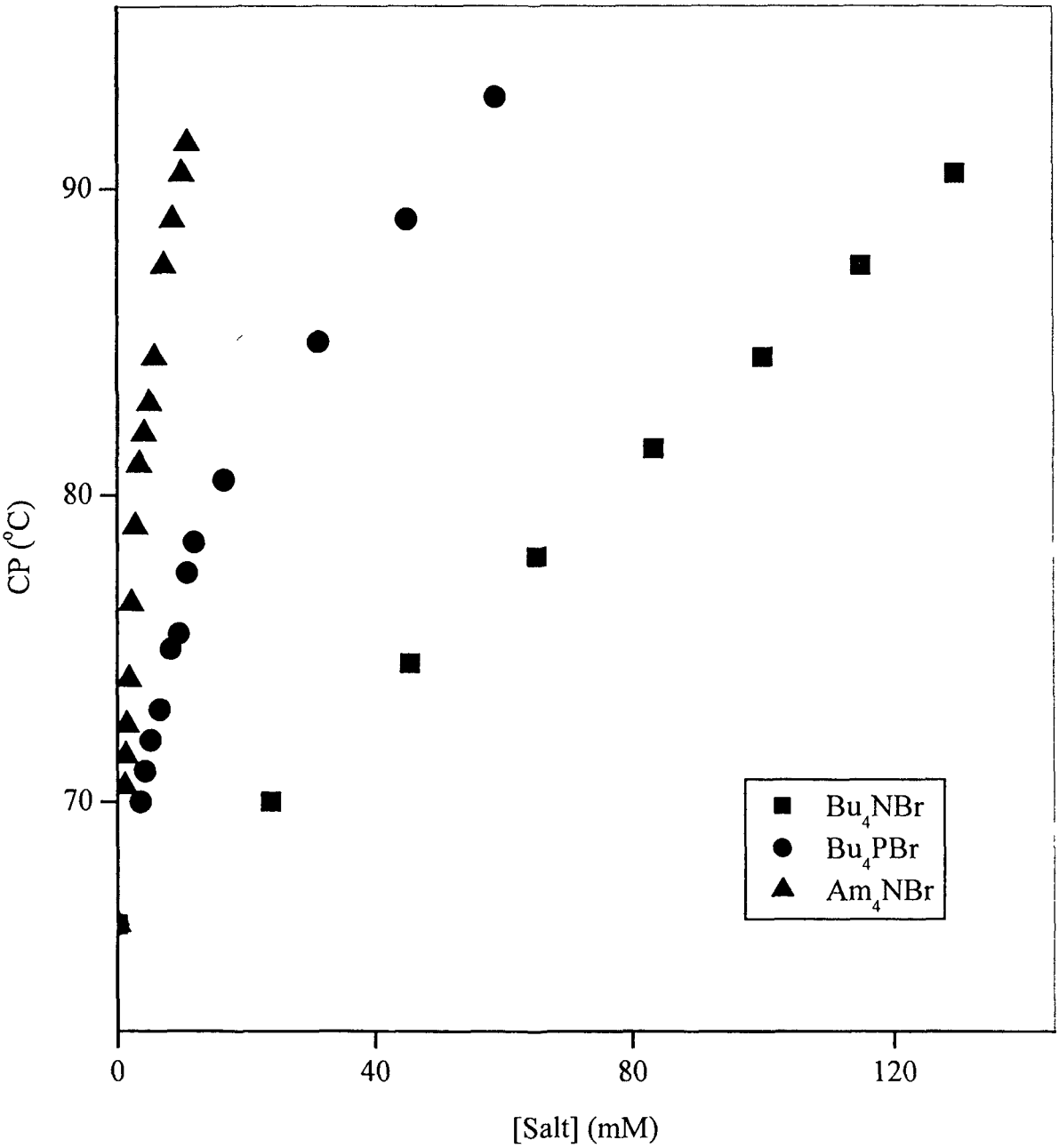


Fig. 3.9 : Variation of Cloud Point with [salt] for 50 mM TX-100.

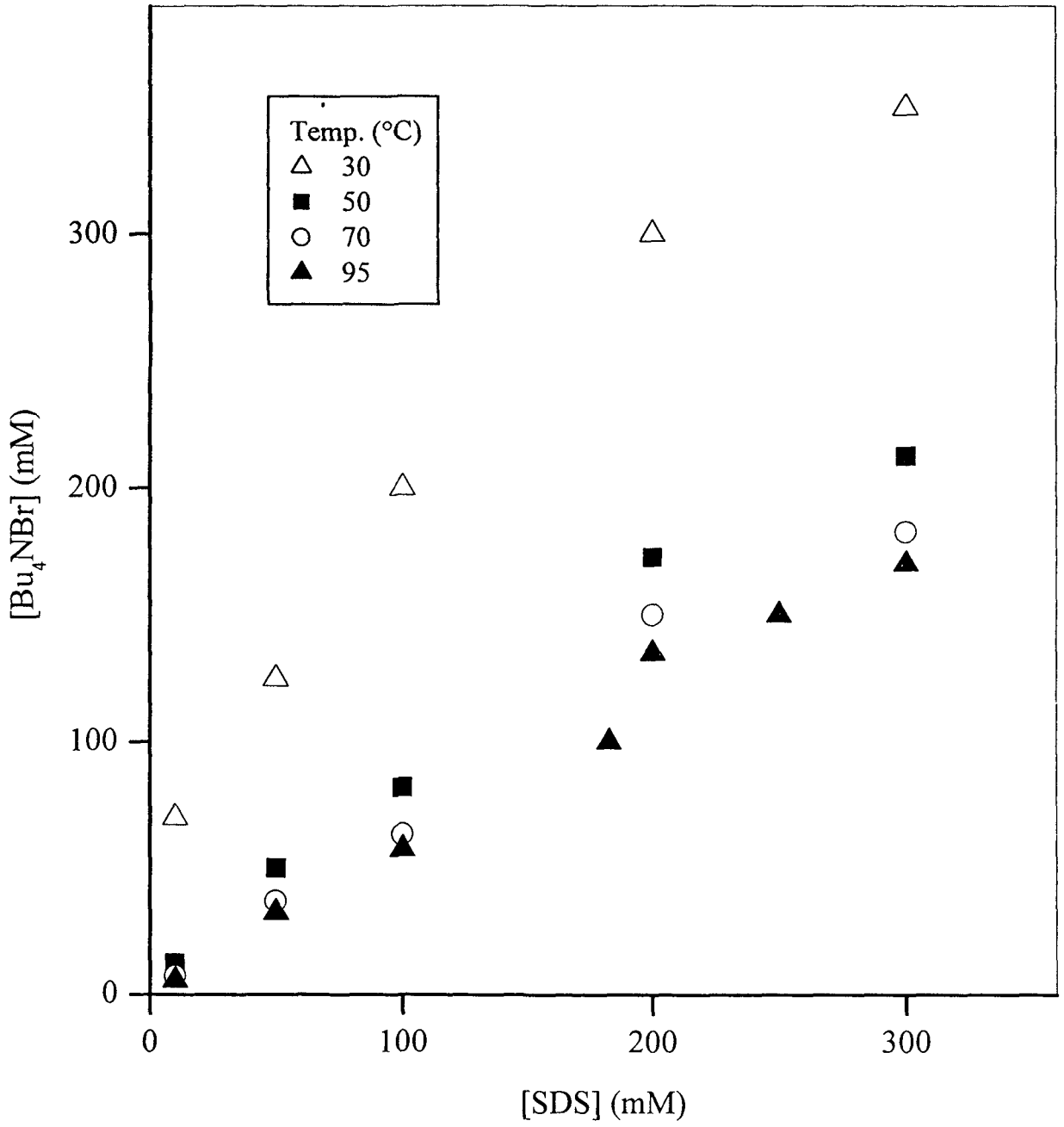


Fig. 3.10 : Plots between [SDS] and [Bu_4NBr] required for the appearance of Cloud Point at different temperatures.

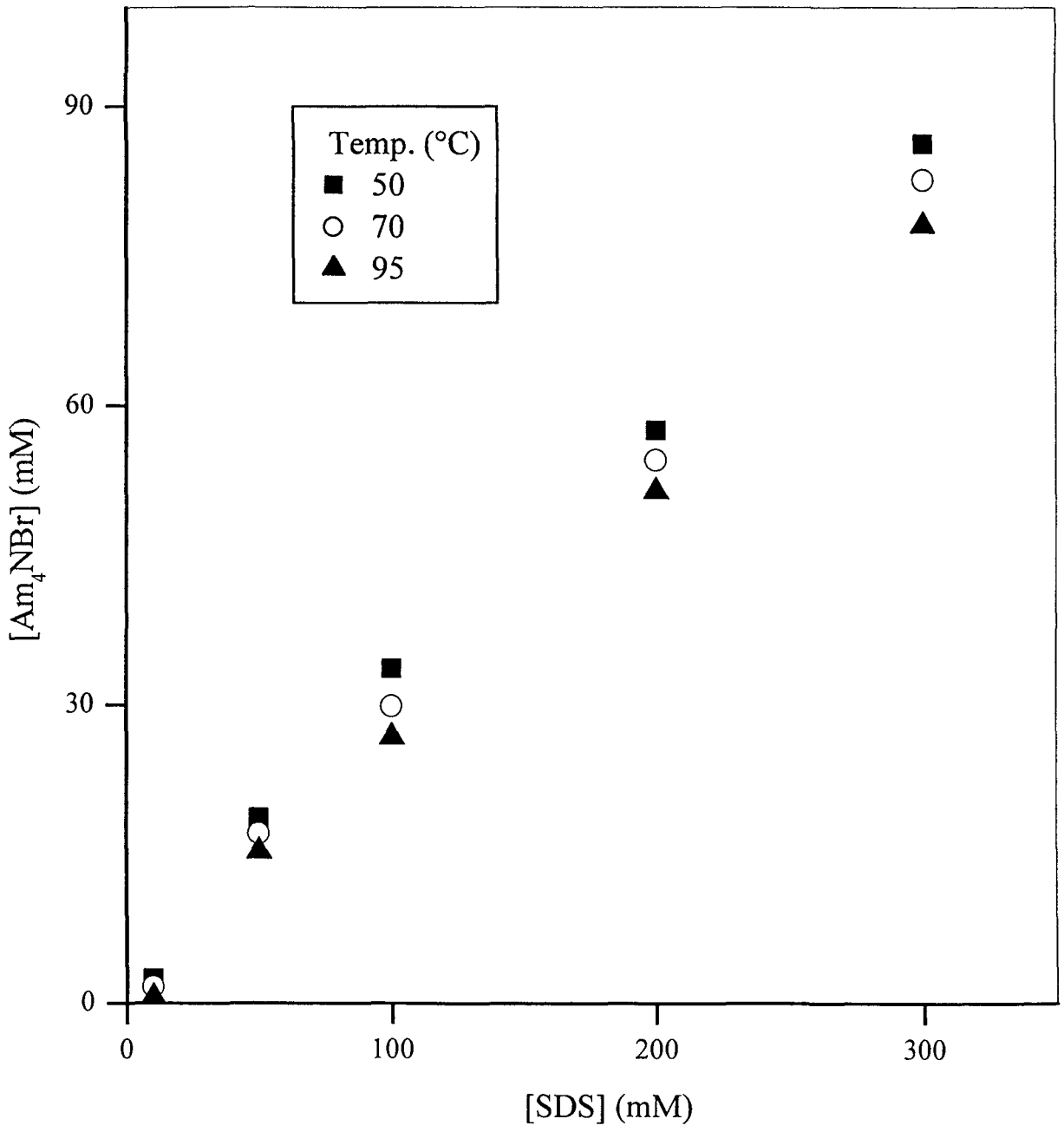


Fig. 3.11 : Plots between [SDS] and [Am_4NBr] required for the appearance of Cloud Point at different temperatures.

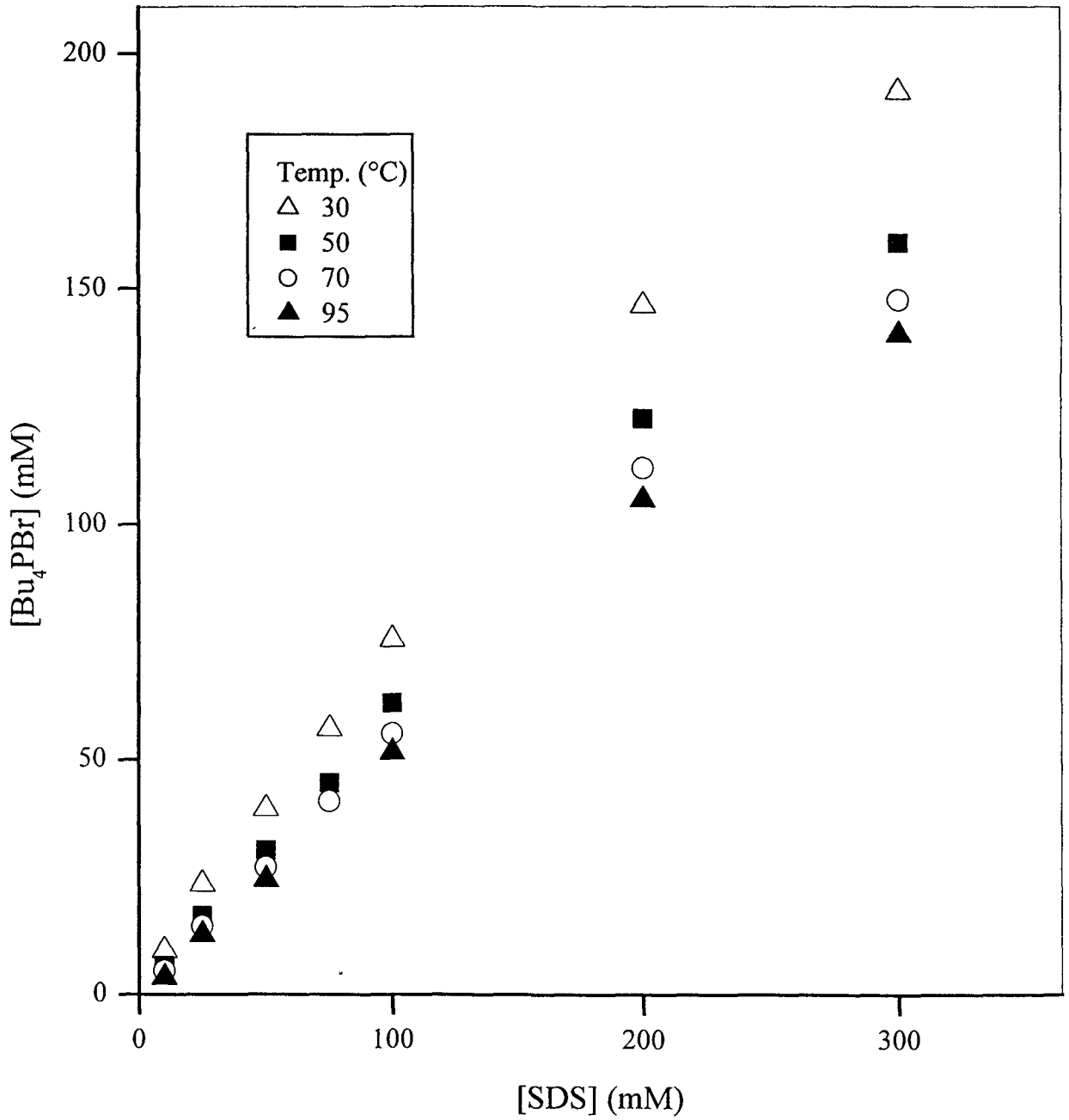


Fig. 3.12 : Plots between [SDS] and [Bu_4PBr] required for the appearance of Cloud Point at different temperatures.

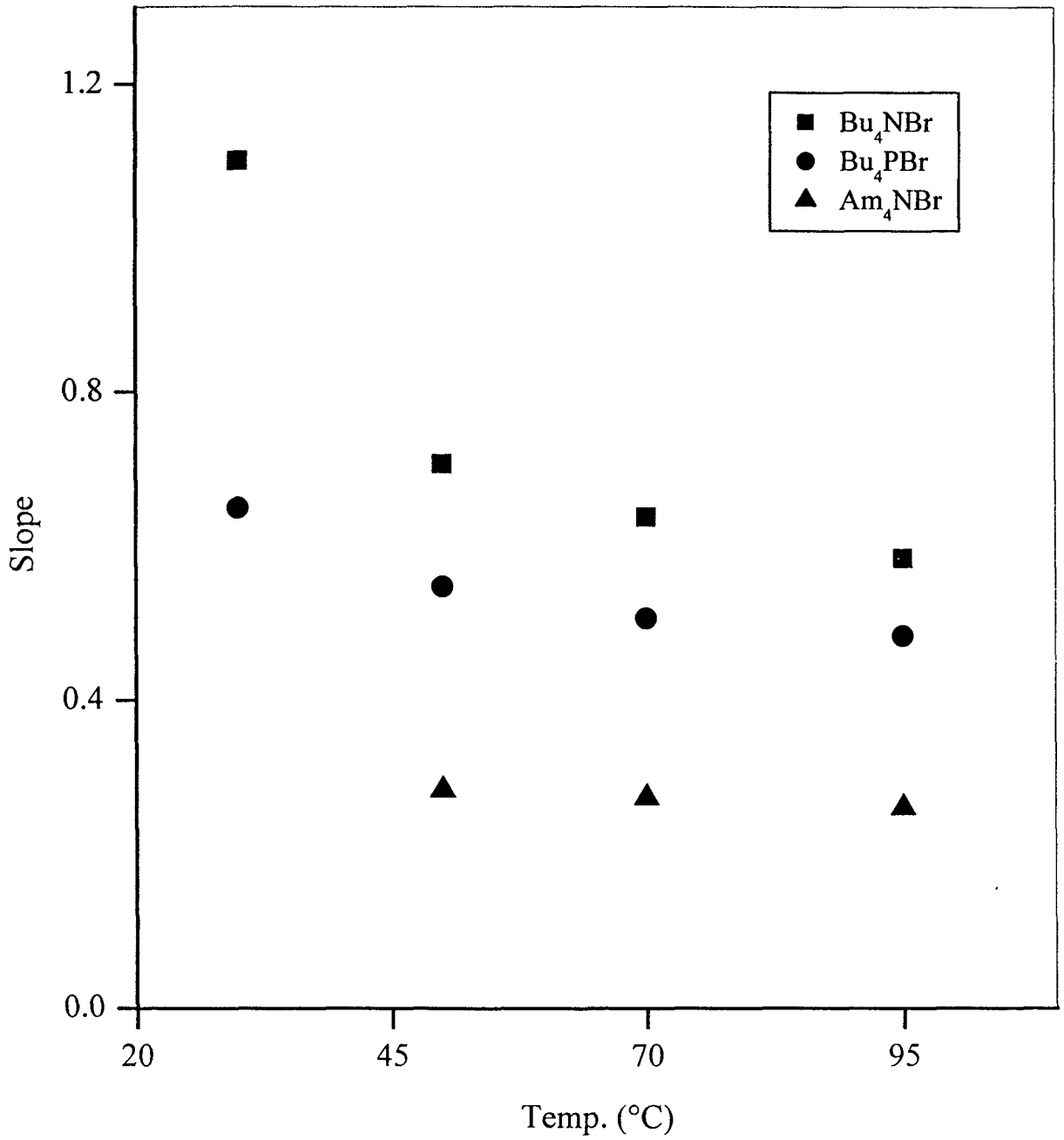


Fig. 3.13 : Variation of [salt] needed per mole of surfactant with temperature.

study[146] with SDS-quaternary bromides, micellar growth was explained in terms of charge neutralization and penetration of few alkyl chains inside the micelle, although exact arrangement of these chains at the micellar surface is yet to be established. In the present context, alkyl chains of such a quaternary counterion (which has four of them and as such alkyl groups possess a large hydrophobic volume) may get embedded between monomers of the micelle due to the hydrophobic effect. But geometric barrier makes it difficult for all the four chains to penetrate into the micellar core. Generally, two directions may be chosen for bending the alkyl chains : one is towards the water phase and the other penetrates the micellar core.[313] In the latter case, the iceberg-like water structure around the alkyl chains penetrating into the micellar core will break down. The alkyl chains towards water phase may have the chance to interact with the alkyl chains of other counterions attached to another micelle. As a result of this, the micelles may experience more close contact. Therefore, in addition to van der Waals attraction, electrical repulsion, and the solvation layer (vide supra), a penetration effect will operate in the present case. Among these forces, van der Waals attraction and penetration effect will assist in attracting two micelles together while electrical repulsion and solvation effect will prevent the micellar contact. A combination of these two categories (which oppose each other) results in an energy barrier between the micelles. As the temperature is raised, the barrier is lowered due to the progressive decrease of structured water on micellar surface.[241] At CP, the barrier becomes sufficiently lower that a collapse of the micelles occurs. Since the number of alkyl chains on the micellar surface are proportional to the salt content in the system, more alkyl chains near the headgroup region will replace more structured water and CP is expected to appear at a lower temperature with the same surfactant

concentration at higher salt contents. This indeed was observed (Figs. 3.1-3.3). As the alkyl chain length in the salt increases, the interaction among the micelles will be stronger due to increased hydrophobic interactions as well as replacement of more structured water with a concomitant appearance of CP at lower concentrations. The above factors seem responsible in making Am_4N^+ more effective in CP lowering of the system (Fig. 3.2). As one moves from Bu_4N^+ to Bu_4P^+, size of the counterion increases with a necessary consequence of removal of more water with increased CP lowering effect (Fig. 3.3). With increase in SDS concentration, the CP starts appearing at higher salt concentration. This may be due to increased number density of micelle at higher [SDS] which can cause decrease in the effective salt content per micelle. As discussed above, the salt content (number of alkyl chains), in addition to other factors, are also responsible for CP appearance. Therefore, at higher [SDS], CP appears at higher concentration of the salt (Fig. 3.4).

Fig. 3.5 shows the conductivity variation for solutions of pure SDS (0.3M), Bu_4NBr (0.2M), and a mixture of SDS (0.3M) and Bu_4NBr (0.2M) with temperature. The conductivity of the system is the sum of the contributions from the micellar aggregates and from the bulk solvent. Interestingly, the conductivity of the mixture is higher than the sum of the conductivities of SDS (0.3M) and Bu_4NBr (0.2M). This means that the concentration of conducting species in the mixture has increased. Since Na^+ ions are highly conducting, their contribution to the total conductance is greater. As Bu_4N^+ interacts with the micellar surface electrostatically and hydrophobically, there is a high possibility of substitution of Na^+ by Bu_4N^+ from the micellar surface.[314] If so, more Na^+ would be in the bulk solvent and the conductivity of the mixture would be greater than the sum

of the individual components. As the temperature increases, the electrostatic and specific[314,315](hydrophobic in this case) interactions between the sulfate headgroup and Bu_4N^+ become stronger with a concomitant reduction in surface hydration with the result that more Na^+ passes out into the bulk solvent. The conductivity data in Fig 3.5 support this point because the increase in mixture conductivity with temperature is greater than that of the constituents.

The increase in turbidity at the cloud point is generally considered to be due to formation of large aggregates. Corti *et al.*[316,317] interpreted the increase in turbidity as due to critical fluctuations of micellar concentrations and not to a temperature dependence of the micellar size. As stated earlier, viscosity measuremants were performed to get an idea of the micellar size and shape.

The viscosity measurements were made at different temperatures for the respective systems as they approach CP (Figs. 3.6-3.8). An interesting feature can be seen that the dependence of η_r on temperature is different from low to high surfactant/salt ratios. At low SDS concentration, the content of quaternary ion in the micelles will be increased with an increase of the salt concentration. Therefore, most of the Na^+ ions will be replaced by quaternary ions, resulting in the Na^+ ions driven off to the beckground solution. These Na^+ ions will screen out the electrostatic interactions and increase simultaneously the size of the micelles, which causes the viscosity to increase (as indeed observed in Fig. 3.6). Fig 3.7 shows the η_r variation for lower salt concentrations, which suggests that sufficient quaternary bromide is not present to replace Na^+ and effective screening does not take place. Similarly, for higher SDS concentrations (Fig. 3.8) the effective salt concentration will decrease, and temperature

has the opposite effect (i.e., decrease in η_r) as most of the Na^+ ions will remain in the proximity of the micellar surface.[318] People have discussed the influence of an excess amount of NaBr on the micellar properties in terms of the competing effect of Na^+ with the adsorption of a quaternary ion on the micellar surface. The present results indicate that the viscosity behavior is dependent on the amount of Na^+ or quaternary ions present at the micellar surface, which will compete for a possible site near the headgroup region. η_r can be described as a product of an increasing and a decreasing function (micellar size and intermicellar interactions, respectively), and the molecular interpretation of this quantity seems quite complicated.[319]

Nonionic TX-100 has its own CP[320] at the concentration used. Contrary to the SDS systems, addition of Bu_4N^+, Am_4N^+ or Bu_4P^+ to solutions of TX - 100 increases the CP (Fig. 3.9) : the order of effectivenes being $Am_4N^+ > Bu_4P^+ > Bu_4N^+$. This may be due to the fact that the hydrophobic nature of these counterions would enable them to interact favorably with TX-100 micelles while a positive charge on them would introduce electrostatic repulsion between the micelles[305] (owing to adsorption at the micellar surface). CP increase has been observed in nonionic surfactant solutions on the addition of different organic acids/ salts and also a few ionic surfactants.[321-323] The increase in CP by quaternary ions is generally considered to be due to the more favorable interaction between water and the polyethylene oxide (PEO) chains.[324] It is further suggested that such salts affect the solvation capacity of water in relation to the PEO units, especially at higher temperatures.[325] To add to this, the present results suggest that solvation capacity of water with respect to PEO is further enhanced with the size of these cations (either due to increase in alkyl chain, as in case of Am_4^+, or due to large central

atom, as in case of Bu_4P^+). The present data could thus be anticipated, and are in consonance with the earlier works.[324-326]

Figs. 3.10 - 3.12 show plots of [SDS] vs. minimum [salt] needed for the appearance of CP at a particular temperature. The plots of Figs. 3.11 and 3.12 demonstrate that for each salt counterion there exists a relationship between [SDS] - [salt] that follows in a wide temperature range with very little positive intercept at lower temperatures. However, the CP data with Bu_4NBr (Fig. 3.10) show a departure from the above trend with a significant positive intercept with bad correlation. The slopes (S) and intercepts (I) together with regression coefficients (r) are summarized in Table 3.13. From the perusal of these data it is clear that, at 95 °C, I is insignificant and S simply represents the minimum [salt] per mole of SDS which is comparatively quite low in case of Am_4NBr. This again confirms that Am_4NBr is more effective in producing CP in SDS micellar solutions. As we see the data of Table 3.13 for lower temperatures, the [salt] needed for CP is increased together with a gradual increase in I. This indicates requirement of extra salt in addition to S. The hydration state of SDS micelles at the ambient temperature and at 95 °C would be different as, at the latter temperature, the micellar interfacial region is nearly completely dehydrated. But, even at such an elevated temperature the size of the counterion has not lost its significance (for example, the data of 50 °C in Table 3.13 reveal that the amount of Am_4NBr needed is quite less as compared to its butyl counterpart). Nearly the same values of S (Table 3.13) obtained for different temperatures with Am_4NBr clarify a bone of contention: *Am_4NBr appears to be a better salt for tuning CP at a desired temperature.*

Fig. 3.13 shows the variation of the amounts of salts per mole of SDS (i.e., slope, S) needed for getting CP with temperature. There exist two separate ranges of temperature in the curves, which indicate that the added of quaternary salt is used not for one single purpose. At lower temperatures, the hydration of micelles becomes important and thus needs an extra salt for lowering the CP per degree of temperature. This allows us to propose that at ambient temperature, the added salt is partly utilized to decrease the hydration and partly to modify the electrostatic/ hydrophobic forces. After a certain temperature (ca. > 50 °C), the hydration becomes less significant and the required salt is utilized mainly to charge depletion and hence a more regular behavior is expected: this is what we see with Am_4NBr (Fig. 3.13).

Chapter - IV

Effect of Additives on the Cloud Point of Sodium Dodecyl Sulfate + Tetra-n-butylammonium Bromide Systems

Introduction

Clouding of surfactants and polymers alone or in mixture has been studied by many workers.[327-329] However, invariably nonionics are not present just by themselves (the cloud points of nonionics are nearly independent of surfactant concentration between < 0.5 and > 5%[330]) and other ingredients such as anionic surfactants and electrolytes commonly present in detergent products strongly affect their clouding behavior.[296]

The effects of different additives on the cloud point behavior of nonionic surfactants have been investigated.[331-333] The additives include anionic surfactants, electrolytes, and hydrotropes. It has been established that salting-out electrolytes lower the cloud point of nonionic surfactants by dehydrating the micelles, leading to the precipitation of surfactant molecules.[139] Salting-in electrolytes work in the opposite way.[331-332] Anionic surfactants form mixed micelles with nonionics and increase the charge repulsion between micelles, thus leading to their stabilization.[332] This results in increased solubility of nonionic surfactant at a given temperature or equivalently, an increase in the cloud point of nonionic solution with a fixed concentration.[304] Hydrotopes gradually increase the cloud point for similar reasons. Extending this logic further, cationic surfactants are also expected to behave in a similar manner since the effect is based on the sign of the charge. This has, indeed, been observed.[332]

According to their effects on the water structure, anions either disrupt or enhance the association of water molecules by hydrogen bonds into flickering clusters, shifting the equilibrium

$$n\ H_2O \rightleftharpoons (H_2O)_n$$

towards the left or the right, respectively. Structure-making anions are small

and/or have multiple negative charges, and generate strong electrostatic fields that not only polarize, immobilize, and electrostrict the adjacent water molecules but induce additional order (entropy loss) beyond the first water layer. Such anions, e.g., OH^-, F^-, SO_4^{2-}, and PO_4^{3-} decrease the CP of nonionics.

Structure breakers disrupt the structure of the surrounding water in all but the immediately adjacent layer and raise the CP.

For ionic surfactants, cloud point variation through additives presently lacks predicting power, therefore, it is important to establish a good CP-database of systems undergoing clouding for their desired modes of applications (e.g., CPEM). This work may prove a step forward to break boundaries between ionic and nonionic surfactants with regard to CP variation with additives. One can also widen the spectrum of the CPEM by including the studied systems discussed herein.

On the basis of the results described in Chapter III, the combination 0.3 M SDS + 0.25 M Bu_4NBr was identified for the purpose to see the effect of different types of additives. The chosen system (CP = 39 °C) has a wider temperature window for making variations below and above the CP. The following additives were used to see the effect :

(i)	Sugars	: D(+)-glucose, D(-)-arabinose, D(+)-xylose
(ii)	Amines	: *n*-hexylamine, *n*-heptylamine, *n*-octylamine
	Alcohols	: *n*-hexanol, *n*-heptanol, *n*-octanol
	Hydrocarbons	: *n*-hexane, *n*-heptane, benzene, toluene, *o*-xylene
(iii)	Amides	: formamide, acetamide, dimethylformamide, salicylamide, urea, tetramethylurea.
	Thioamides	: thioacetamide, thiourea, tetramethylthiourea
(iv)	Acids	: malic acid, thiomalic acid

(v) Salts : sodium nitrate, sodium sulfate, sodium orthophosphate, guanidine hydrochloride, thiamine hydrochloride

(iv) Organic solvents : ethylene glycol, propylene glycol, dioxane, dimethylsulfoxide

Results

Tables 4.1 - 4.8 record the CP values of the system 0.3 M SDS + 0.25 M Bu_4NBr as a function of the concentration of various additives. The results are shown graphically in Figs. 4.1-4.6.

Discussion

The dependence of micellar solubilization on temperature depends on the structure of the solubilizate and surfactant, and in most cases increases with increasing temperature. The effects can generally be ascribed either to (i) a change in the aqueous solubility of the solubilizate and (ii) a change in the properties of the micelles. Since solubilization increases as the temperature approaches the cloud point, the effect of the solubilizate itself on the cloud point is of paramount importance. Conversely, the effect of the solubilization on the cloud point provides an indication of the location and maximum solubilization. In general, aliphatic hydrocarbons raise the CP while aromatic and polar solutes tend to lower it in nonionic surfactants. Similarly, phenols sharply decrease the cloud point of nonionics.[334,335] Solutes which decrease the cloud point do so by solubilizing in the POE mantle of the micelle. Interaction with the EO groups causes dehydration and thus phase separation.

As pointed out by Schott,[336] many salts raise the CP of nonionics so that this may be more the rule than the exception. A scheme has been given to understand the basis of the effect of salts on CP. A summary of the

Table 4.1 : Cloud Point (^{0}C) variation in the system 0.3 M SDS + 0.25 M Bu_4NBr with the concentration of various sugars.

	CP		
[Sugar](M)	D(+)-Glucose	D(-)-Arabinose	D(+)-Xylose
0.0	39.0	39.0	39.0
0.083		36.3	
0.100	37.4		
0.116		36.3	
0.139			37.0
0.198		35.4	
0.199			36.3
0.250	36.4		
0.283		34.4	
0.290			35.8
0.387			35.0
0.396		33.2	
0.470		38.1	
0.498			34.1
0.500	34.6		
0.542		31.0	
0.637		29.7	
0.697			32.5
0.698		28.6	
0.750	28.3		
0.811			31.9
0.937			30.5
1.000	26.5		
1.154			28.0
1.363			25.8
1.579			24.0

Table 4.2 : Cloud Point (^{0}C) variation in the system 0.3 M SDS + 0.25 M Bu_4NBr with the concentration of organic additives.

[Additive] (M)	CP	[Additive] (M)	CP
0.0	39.5		
C_6OH		**C_6NH_2**	
0.05	32.2	0.05	37.8
0.10	27.6	0.10	36.1
C_7OH		**C_7NH_2**	
0.05	31.0	0.05	36.7
0.10	25.1	0.10	34.4
C_8OH		**C_8NH_2**	
0.05	30.0	0.05	36.3
0.08	22.1	0.10	33.5
C_6H_{14}			
0.05	37.6		
0.10	36.9		
C_7H_{16}			
0.06	36.0		
0.11	33.8		

Table 4.3 : Cloud Point (^{0}C) variation in the system 0.3 M SDS + 0.25 M Bu_4NBr with the concentration of aromatic hydrocarbons (AH).

[AH] (M)	CP		
	Benzene	Toluene	*o*-Xylene
0.0	39.0	39.0	39.0
0.05	34.8	34.0	32.5
0.10	30.5	29.4	27.5
0.15	24.5	24.6	22.4
0.20	23.5	23.0	18.0

Table 4.4 : Cloud Point (^{0}C) variation in the system 0.3 M SDS + 0.25 M Bu_4NBr with the concentration of amides.

	CP			
[Amide] (M)	**Formamide**	**N,N-Dimethyl-formamide**	**Acetamide**	**Salicylamide[a]**
0.0	39.0	39.0	39.0	39.0
0.10	39.6	40.3	40.0	34.7 (0.010M)
0.25	39.6	41.3	40.5	32.3 (0.015M)
0.50	39.2	43.9	43.2	29.7 (0.020M)
1.00	38.7	47.3	46.2	27.8 (0.025M)
1.25			56.0	25.5 (0.030M)
1.50	37.5	51.5	65.0	24.1 (0.035M)
				23.2 (0.040M)

[a]The concentrations of added salicylamide (in parentheses) were different than that of the other amides.

Table 4.5 : Cloud Point (^{0}C) variation in the system 0.3 M SDS + 0.25 M Bu_4NBr with the concentration of oxy compounds.

[Additive] (M)	CP		
	Urea	Tetramethylurea	Malic acid
0.0	39.0	39.0	39.0
0.10	39.8	41.0	38.0
0.25		44.5	36.5
0.50	42.9	48.6	34.5
0.75		54.6	
1.00	45.0	62.0	33.0
1.50	50.0		

Table 4.6 : Cloud Point (^{0}C) variation in the system 0.3 M SDS + 0.25 M Bu_4NBr with the concentration of thio compounds.

[Additive] (M)	CP			
	Thiourea	Tetramethyl thiourea	Thiomalic acid	Thioacetamide
0.0	39.0	39.0	39.0	39.0
0.010			25.0	
0.015				38.6
0.020			22.0	38.1
0.030			19.5	37.3
0.050			17.0	
0.100	34.9	38.9		
0.250	30.7	36.1		
0.375	24.8			
0.500		34.0		
0.750		30.0		
1.000		24.5		

Table 4.7 : Cloud Point (°C) variation in the system 0.3 M +0.25 M Bu_4NBr with the concentration of various organic solvents.

[Additive] (M)	CP			
	Ethylene Glycol	Propylene Glycol	Dioxane	Dimethyl Sulfoxide
0.0	39.0	39.0	39.0	39.0
0.10	39.6	39.6	39.6	40.3
0.25	39.6	39.8	40.4	41.3
0.50	39.8	40.2	42.0	43.9
1.00	40.0	40.8	44.7	47.3
1.50			45.9	51.5

Table 4.8 : Cloud Point (^{0}C) variation in the system 0.3 M SDS + 0.25 M Bu_4NBr with the concentration of a few organic and inorganic salts.

	CP				
[Salt](M)	$NaNO_3$	Na_2SO_4	Na_3PO_4	T.HCl	Gu.HCl
0.0	39.0	39.0	39.0	39.0	39.0
0.005					35.9
0.008					31.6
0.010		37.6		38.5	
0.021		37.0			
0.025		36.6			
0.036		35.5			
0.046		34.5			
0.050	38.0			34.1	
0.058		33.4			
0.073		32.3			
0.083		31.9			
0.100	37.5		36.4	31.2	
0.106		29.5			
0.125			34.0		
0.135		27.5			
0.150			31.0	29.5	
0.161		26.5			
0.178		25.5			
0.200		24.0	26.0	27.8	
0.217		22.0			
0.225			20.0		
0.250	37.0		15.0		
0.500	36.0				
0.833	35.0				
1.000	34.0				

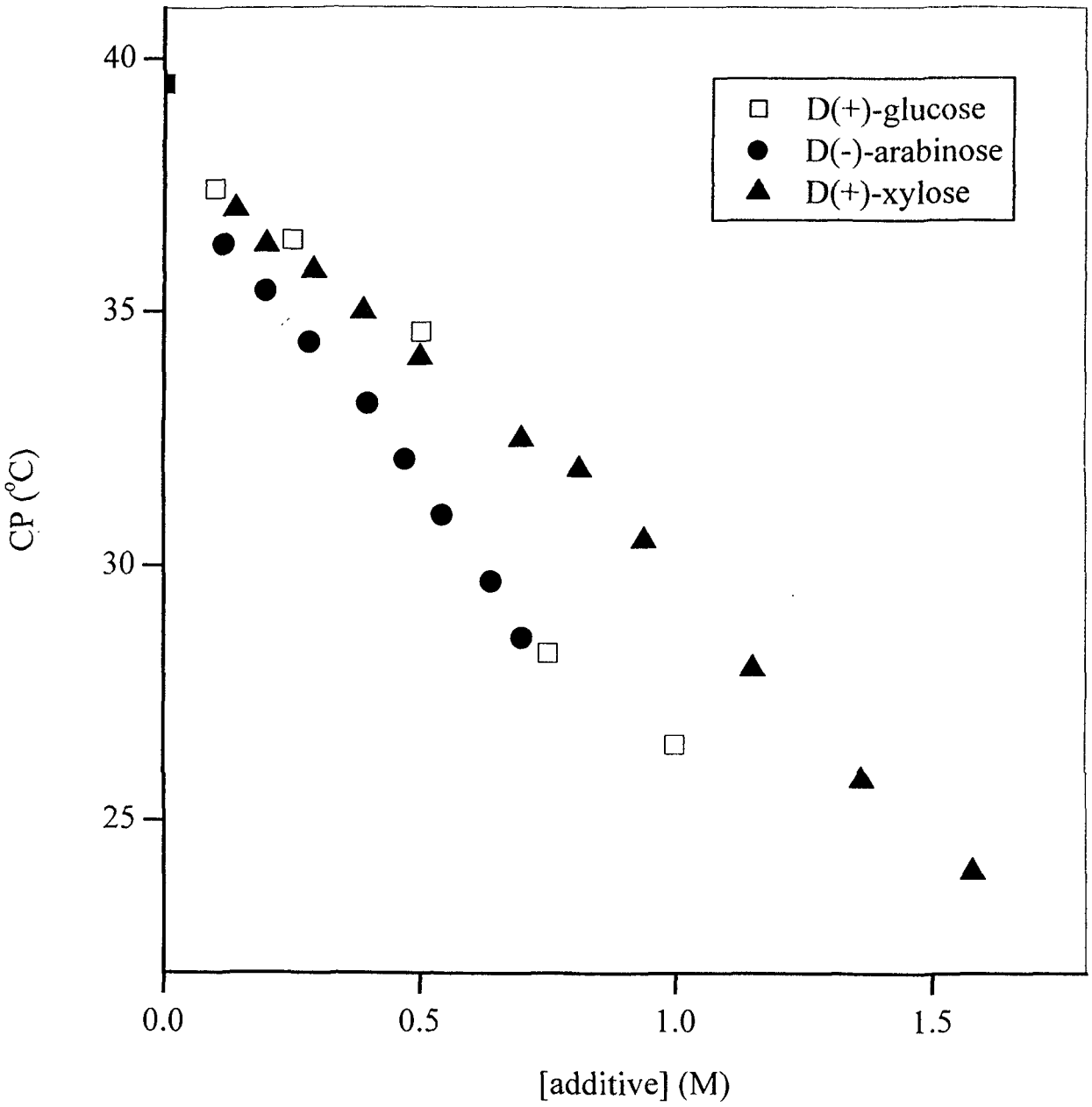


Fig. 4.1 : Variation of Cloud Point with [sugar] for the 0.3 M SDS + 0.25 M Bu_4NBr system.

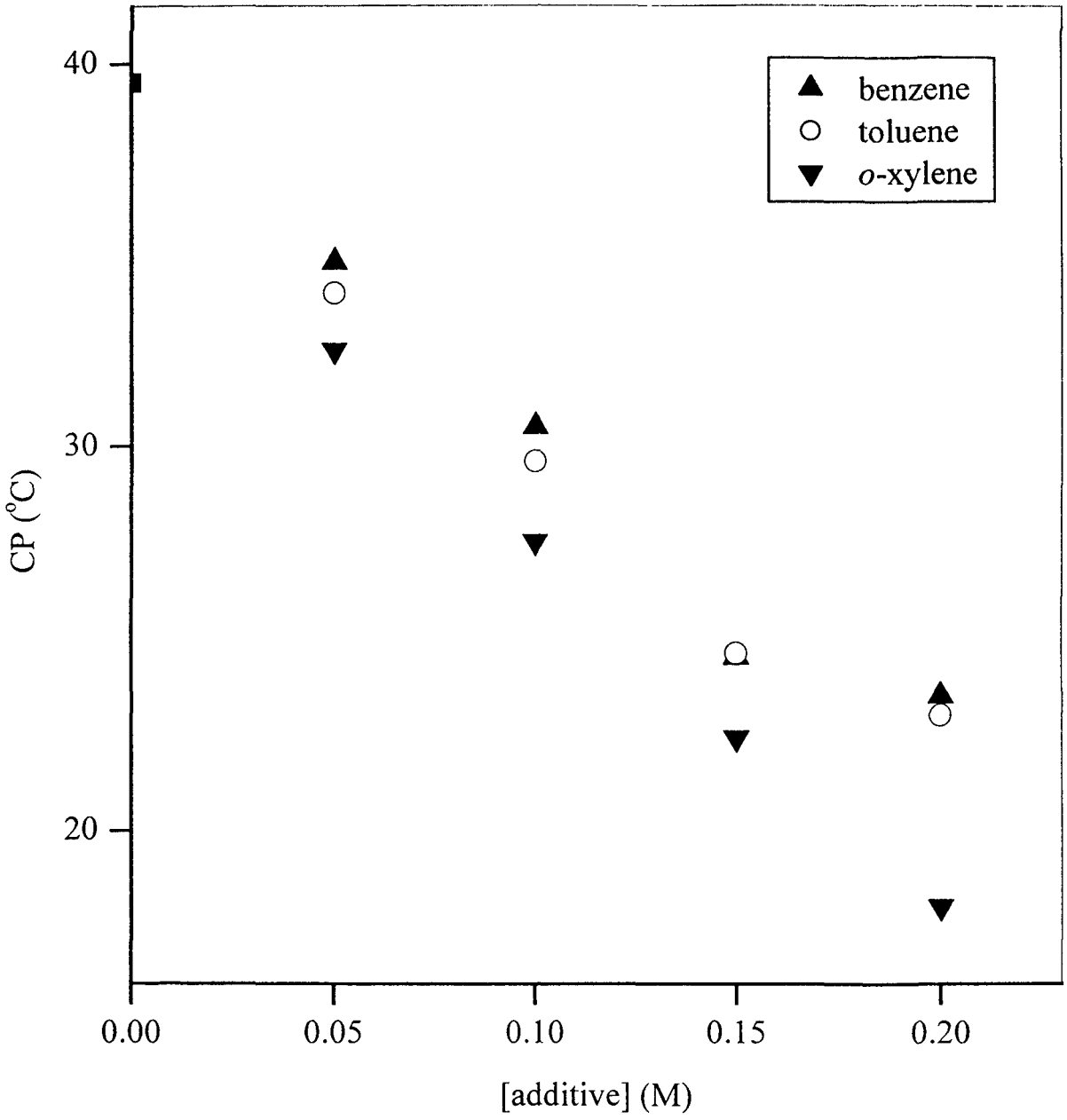


Fig. 4.2 : Variation of Cloud Point with [aromatic hydrocarbon] for the 0.3 M SDS + 0.25 M Bu_4NBr system.

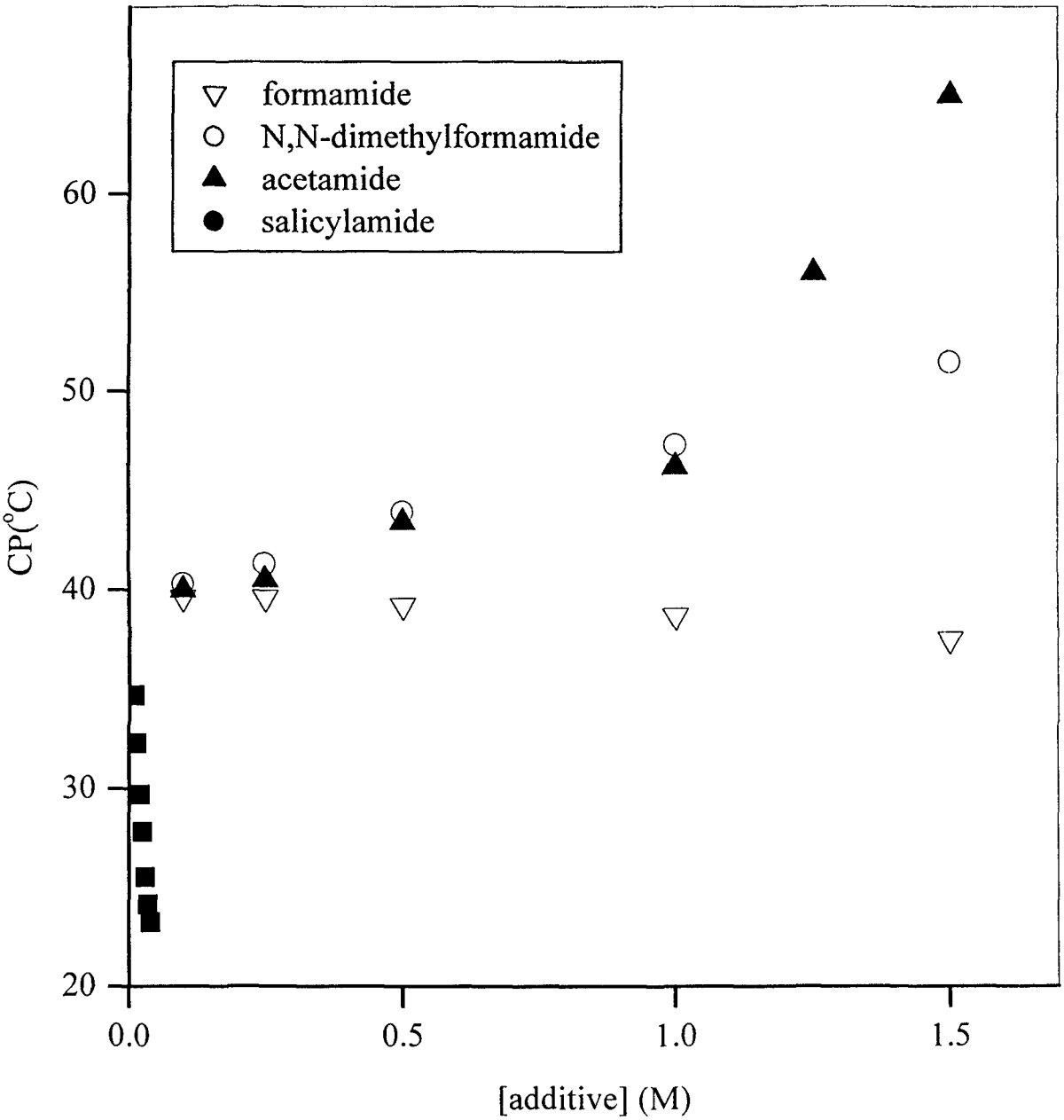


Fig. 4.3 : Variation of Cloud Point with [amide] for the 0.3 M SDS + 0.25 M Bu_4NBr system.

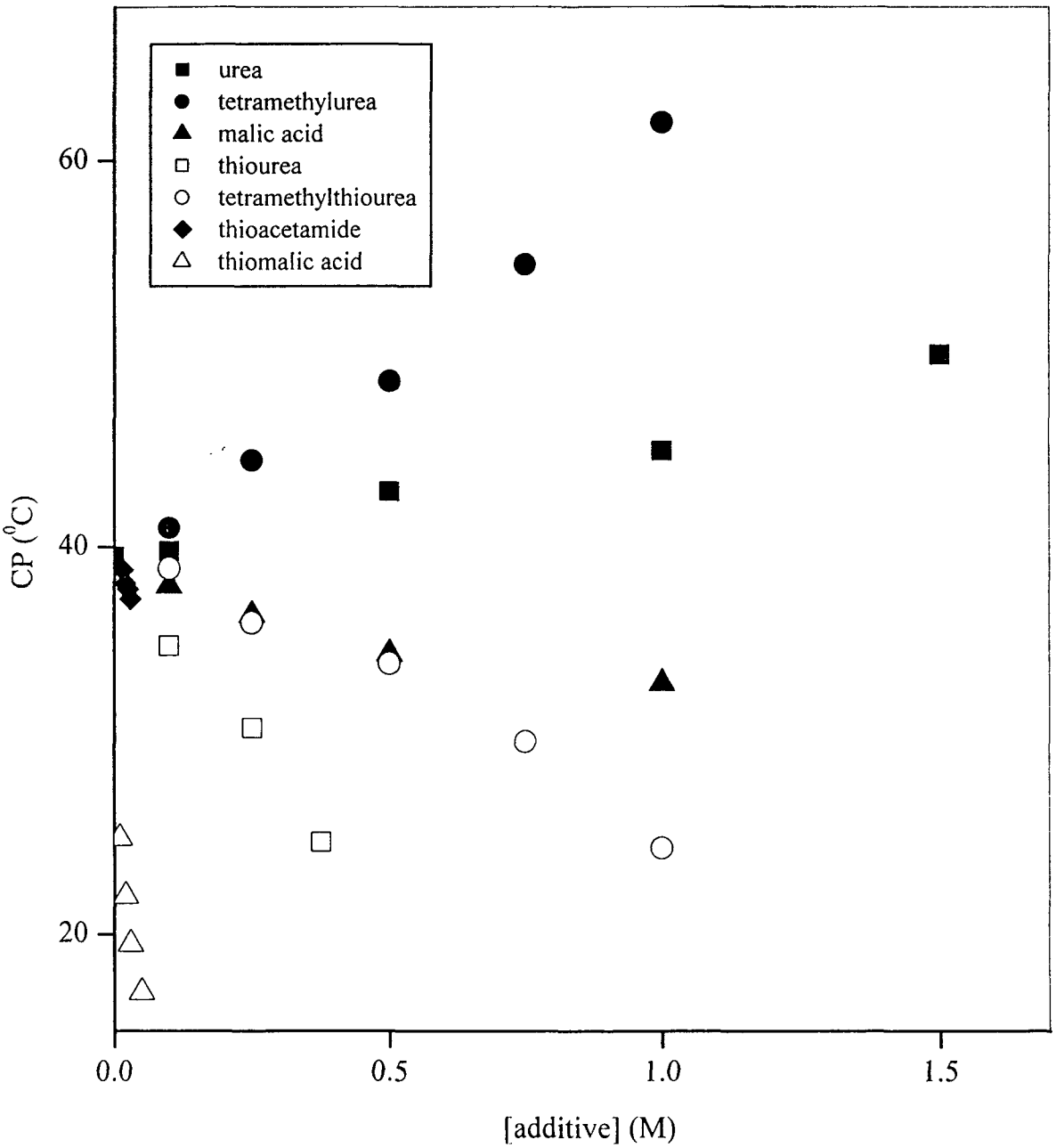


Fig. 4.4: Variation of Cloud Point with [additive] for the 0.3 M SDS + 0.25 M Bu_4NBr system.

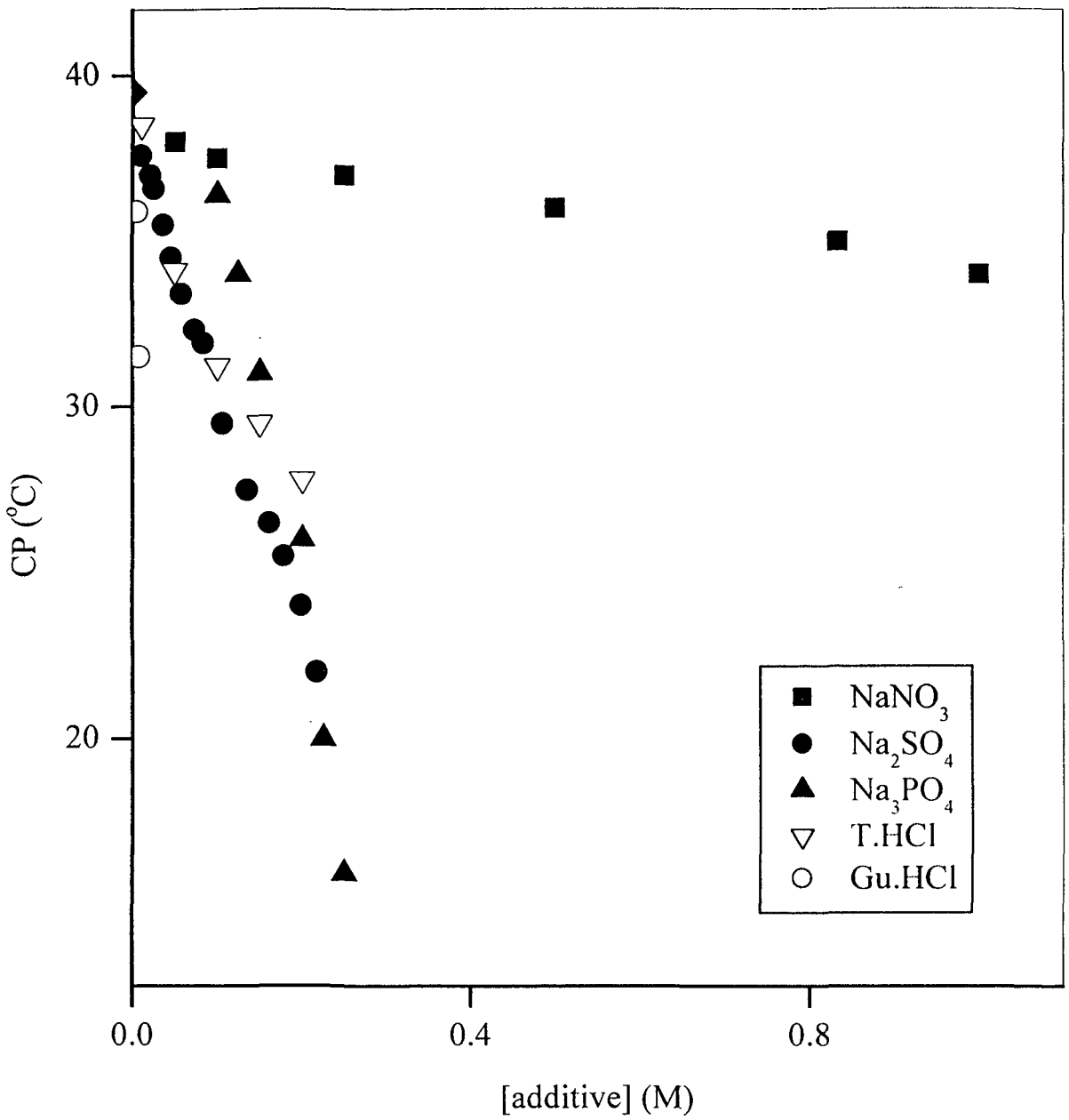


Fig. 4.5: Variation of Cloud Point with [salt] for the 0.3 M SDS + 0.25 M Bu_4NBr system.

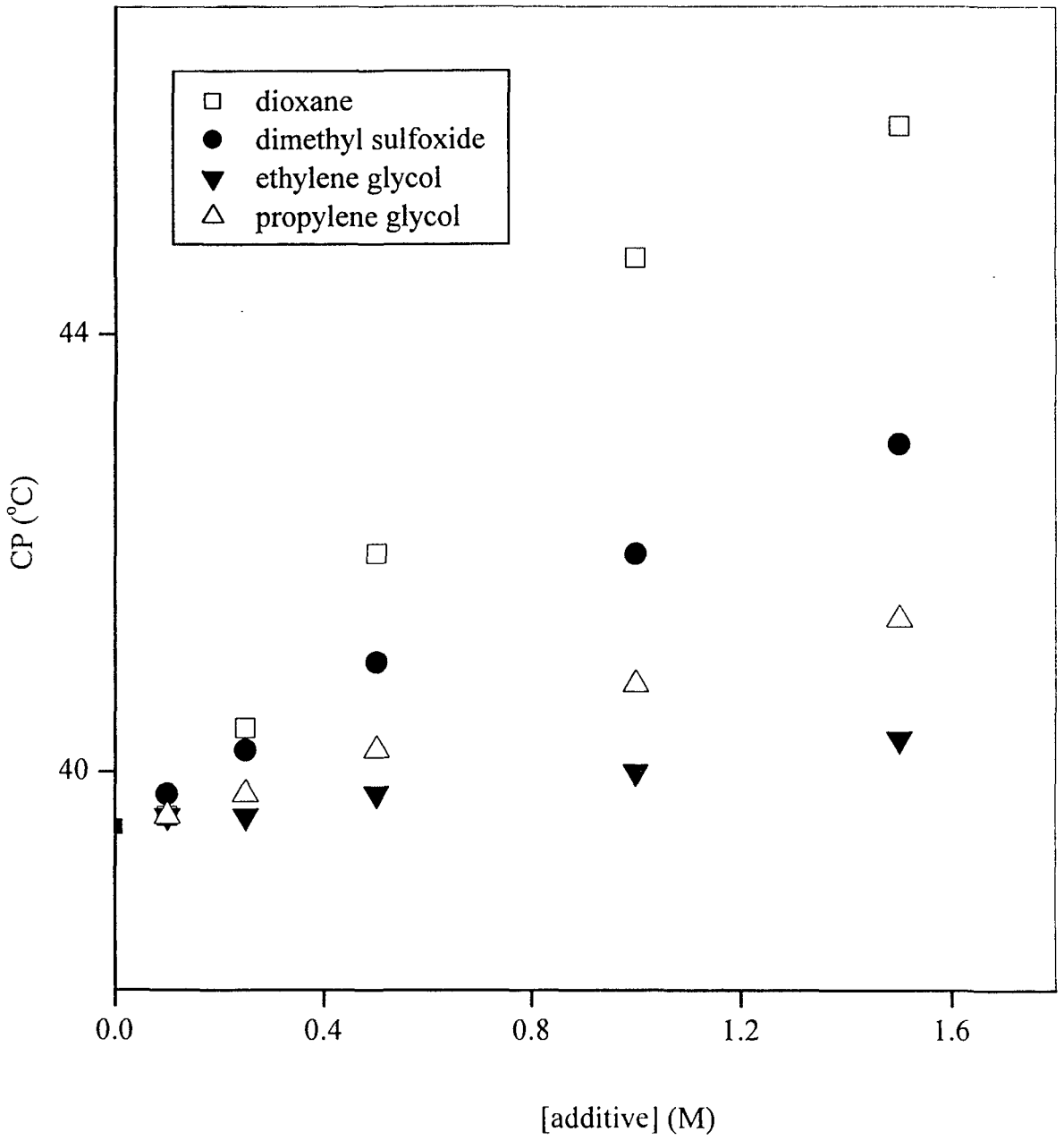


Fig. 4.6: Variation of Cloud Point with [solvent] for 0.3 M SDS + 0.25 M Bu_4NBr systems.

effects of various anions and cations, relative to nitrate as the (zero point) reference for different nonionic surfactants, is given.[139] The above facts can be used to explain the changes in CP which occur with various additives.

Fig. 4.1 shows the effect of adding sugars on the CP variation of 0.3 M SDS + 0.25 M Bu_4NBr system. The addition of each compound of this category produces a decrease in the CP. These observations are similar in form to the decrease in the water solubility of hydrophobic derivatives caused by sugars and reinforce the belief that 'water structure makers' strengthen hydrophobic interactions. The CP depression indicates a 'salting-out' effect because the temperature range in which the single phase solutions prevail is reduced. It has been reported that sugars promote water structure and so decrease the CMC of surfactants.[167]

Table 4.2 shows that though a decrease in the CP is observed with all the additives (aliphatic alcohols, amines, hydrocarbons), the rate is the highest with alcohols. Polar organic compounds are known to usually partition in the headgroup region with the alkyl chain penetrating into the micellar core. This partitioning would replace the amount of water near the headgroup region with a lower temperature required to obtain the CP phenomenon. The hydrophilic ranking was discussed by Wormuth and Kaler[337] for a few polar organic compounds and they suggested that amines were more hydrophilic than alcohols. Amines will, therefore, replace less water from the headgroup region than alcohols -- so the CP decrease is more with the latter. Aliphatic hydrocarbons usually partition inside the micellar core and are less effective in replacing water from the headgroup region and hence have a lower effect on decreasing the CP (Table 4.2). However, increasing the alkyl chain length of the polar organic compounds has a distinct effect on the CP, which is due to the replacement of more

water from the micellar surface. It is worth mentioning that in case of nonionics, aliphatic hydrocarbons raise the CP while other polar compounds have decreasing effect by getting solubilized in the POE mantle of the micelle.[324]

A few aromatic hydrocarbons were also tested to determine their effect on the CP of the SDS (0.3 M) + Bu_4NBr (0.25 M) system. We see that the CP decreases with all the aromatic hydrocarbons (Fig. 4.2) with the rate being highest in case of *o*-xylene. The presence of an aromatic hydrocarbon in the system appears to falicitate further removal of the remaining water from the headgroup region.[241] As a result, CP appears at a lower temperature than when the system contains only Bu_4NBr (0.25 M). *o*-Xylene has the highest molar volume and, therefore, at equal [hydrocarbon], CP appears at the lowest temperature in its presence (Fig. 4.2). Rosen[51] suggested that additive size (i.e., its molar volume), polarity, location, and its concentration all influence the solubilization capacity of micelles.

To differentiate between the structure breaker and structure maker type of additives, effect of several oxy and thiocompounds (amides, ureas and acids) on the CP of the chosen system was studied. It is interesting (and surprising too) to observe that most of the amides increase the CP while the analogous thiocompounds produce decreasing effect (Figs. 4.3 and 4.4).

The nature of the solvent affects the dissociation to a marked degree. It weakens the electrostatic forces of attraction between the charges and separates them. This effect of the solvent is measured by its dielectric constant. Solvents affect the CP by modifying the structure of water, its dielectric constant, or its solubility parameter (cohesive energy density). The order of dielectric constant is : formamide > H_2O > acetamide > N,N-dimethylformamide.[338] This order clearly shows that formamide should

behave opposite to other amides. This indeed is observed in Fig. 4.3. However, a sharp decrease in CP is observed with salicylamide. Presence of an aromatic moiety seems to enable salicyclamide to interact hydrophobically with the SDS micelle with a concomitant decrease in CP.

Ureas and thioureas, believed to be structure breakers, increase the CP of nonionic surfactants.[339,340] Several studies have been performed to check the effect of urea as an additive on the properties of micellar solutions[152], and on the denaturation of proteins.[340] Two different mechanisms for urea action have been proposed : (i) urea changes the "structure" of water to facilitate the solvation of a hydrocarbon chain; (ii) urea replaces several water molecules that solvate the hydrophobic chain and the polar headgroup of the amphiphile. The first mechanism is widely accepted and many experimental results seem to support the hypothesis that urea acts as a "water structure breaker".[341] In particular, the addition of urea to surfactant solutions leads to an increase of the CMC value. Jencks and co-workers[342,343] have proposed that the increased solubility of hydrocarbons in aqueous urea results primarily from a smaller free energy of cavity formation in the mixed solvent, resulting from the replacement of water by larger urea molecule in the solvation region. It has also been reported that the counterion dissociation degree (β) of micelles increases with urea addition.[344] As a result of increase of β, the micelle hydration would increase, which would contribute toward the CP increase. Another factor is the solubility increase of surfactant (with urea addition) in the bulk solvent. The two factors taken together would need extra heating in order to observe clouding, and hence the temperature where the surfactant solubility would decrease drastically in the bulk solvent, viz. CP, would be higher. The above observations can be rationalized in terms of competing attractive van der

Waals and repulsive steric interactions between the hydrated micelles. In the present case, the latter effect seems responsible for the increase of CP with ureas. Because of the presence of additional methylene groups in tetramethyl urea, the steep rise in CP may be due to enhanced solubility of nonpolar parts of SDS monomer and Bu_4NBr. The resultant stabilized system (due to enhanced solubility) will obviously show a higher CP. These results corroborate the influence of the presence of additional methylene group in ureas on CMC variation which shows an increasing trend as the number of methylene groups increase.

The interesting behavior of CP decrease in the presence of thiocompounds could be understood in the light of direct interaction of thiocompounds and SDS + Bu_4NBr mixed micelles. The opposite effect of thiocompounds in our case may be due to the difference in the nature of >C=S and >C=O bonds : the >C=O is stronger than >C=S as O atoms are more electronegative. Therefore, electrons around the S atom will be delocalized, thus making the S atom electron deficient, i.e., a Lewis acid. As a result, thiocompounds may have a tendency to interact with the SDS micelle (an anionic centre)[345], and the effect of thiocompounds would be similar to that of quaternary cations, i.e., a CP-decreasing effect. The CP-decreasing effect of malic and thiomalic acids (the effect being more pronounced with the latter) can also be understood in terms of the above facts.

Fig. 4.5 depicts the effect of various salts on the CP of the chosen system. All the salts are found to decrease the CP. The salts provide additional counterions (Na^+, TH^+, GuH^+, etc.) to the system and enhance the counterion binding. Due to this, water of hydration gets removed from the head group resulting in a decrease in CP. The CP decrease with TH^+ is

higher than with the other inorganic counterions. TH^+ is known to interact with SDS micelle electrostatically.[346] In addition to the electrostatic, there is also a possibility of hydrophobic interaction between the non-polar moieties of the two large ions. These two factors taken together would be responsible for decreasing the CP effectively. GuH^+ decreases the CP most effectively. Guanidinium cation (GuH^+) is a known strong water structure breaker (increases the CP of nonionics).[339] Further, this ion takes coplanar, resonance structures and possesses high polarizability.[347] These effects, in a way, would affect the interactions of GuH^+ with micelles and therefore be responsible for CP-decrease.

The organic solvents dioxane, DMSO, ethylene glycol and proplylene glycol are found to increase the CP (Fig. 4.6). The dielectric constants of all these solvents are lower than water and therefore, water + additive would have lower polarity than that of pure water. An increase in CMC of ionic surfactants is observed with these solvents[168,169] as they decrease the cohesive energy density or solubility parameter of the water, thus increasing the solubility of the monomeric form of the surfactant. This would need extra heating in order to observe clouding and hence the CP would be higher. The rate of increase of CP is the highest with dioxane. The retardation effect of dioxane on sphere-to-rod transition for SDS + *n*-pentanol micelles[348] taken together with the fact that dioxane is a water structure breaker are in consonance with the present CP increasing effect. Due to the presence of extra methylene group propylene glycol is more effective than ethylene glycol in increasing CP.

Chapter – V

^{1}H NMR Study on Cetyltrimethylammonium Bromide + Sodium Anthranilate Systems

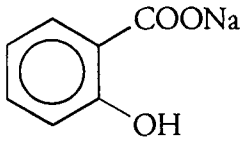
Introduction

Certain surfactants form rod-like or thread-like micelles at higher concentrations or when a second oppositely charged surfactant, organic or inorganic counterion, or uncharged compound is added.[146,310,349] A few of such solutions also show unique viscoelastic behavior.[230,349,350] In any case, the structure of the added molecule is of crucial importance for occurrence of the phenomenon of viscoelasticity.[268,351,352] According to the generally agreed upon model,[319] the viscoelastic effect arises due to the formation of elongated cylindrical micelles, and the resultant systems have a gel-like structure in solutions. However, no clear explanation exists as to why the viscoelastic effects are caused by only a few additives. Elongated micelles of alkyltrimethylammonium and alkylpyridinium salts are typical examples, and these salts have been investigated in detail by various methods, including ^{1}H NMR.[351,353,354]

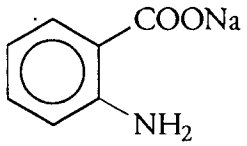
Sodium salicylate (I) and salicylic acid (2-hydroxybenzoic acid) are almost equally effective in driving the spherical-to-cylindrical micelle transition, whereas 3-hydroxybenzoic acid is less effective.[351,355] It has been concluded that as the hydroxy group moves around the benzene ring away from the acid group, the hydrophobic part of the benzene ring is shielded more effectively, and the acid becomes less effective in driving the transition because the phenyl moiety does not penetrate well into the hydrophobic region of the surfactant monolayer.[349] Rehage and Hoffmann[352] have demonstrated that a methyl group in the 4-position of sodium benzoate gives solutions with high viscosities. Further, it has been shown that as the methyl group moves around the benzene ring near the acid group, the solutions exhibit less viscosity and eventually show pure Newtonian flow properties. Replacement of a methyl by an ethyl group at

the 4-position gives an even more pronounced effect. Similarly, it has been observed that a –Cl group at the 4-position is equally as effective as an –OH group at the 2-position (in the case of sodium salicylate).[228] It is clear from the observations that an –OH group is effective at the 2-position, whereas $-CH_3$ or –Cl is effective at the 4-position in initiating the viscoelasticity in the cationic surfactant solution.

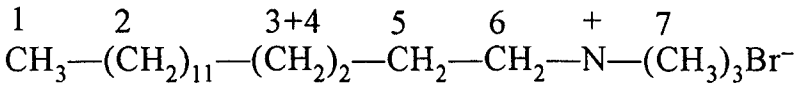
From a chemical point of view, the salicylate anion may show complicated adsorption properties. Considering the polar hydrogen bonds between the -OH group and the neighbouring acid group, other types of interactions can eventually influence the specific orientation at the micellar surface. To understand this complicated phenomenon, it is necessary to investigate other counterions with similar chemical structures. Sodium salts of 2-hydroxybenzoic (sodium salicylate, I), and 2-aminobenzoic acids (sodium anthranilate, II) compare well; therefore, ^1H NMR was used to study the addition of NaAn to cetyltrimethylammonium bromide (III) solutions.



(I)



(II)



(III)

Results

Table 5.1 shows ^1H chemical shifts (δ) data of various protons of 10mM CTAB using D_2O as solvent. The δ values for such protons in presence of various concentrations of the added NaAn are also recorded in Table 5.1.

^1H NMR spectrum for pure 10mM CTAB is shown in Fig. 5.1. Fig. 5.2 illustrates the spectra of 10mM CTAB containing 10mM sodium anthranilate. ^1H NMR spectra of aromatic regions of pure sodium anthranilate and the solutions of 10mM CTAB with varying concentrations of the salt are depiected in Fig. 5.3.

Discussion

Since the reported concentration of CTAB here is about 10 times higher than its critical micelle concentration (CMC), the observed chemical shifts, δ (Table 5.1), can be considered those of micellized surfactant. Fig. 5.1 shows the spectrum of pure 10 mM CTAB solution in D_2O. The main features and peaks are the same as reported previously.[228,351,356] Fig. 5.1 shows that lines 2 and 3+4 corresponding to $(CH_2)_{11}$ and $(CH_2)_2$ of the $(CH_2)_{13}$ hydrocarbon change with δ of 1.25 and 1.31 ppm, respectively. The line 3+4 occurs at higher δ due to the proximity of the $-N(CH_3)_3$ group in the polar headgroup of the surfactant. This identification is important, as will be seen later, in that on interaction of An^- with the micelle lines shift to lower δ (higher field) indicating the presence of the ion in the micellar vicinity. ^1H chemical shifts of the CTAB monomer are shifted upfield on addition of NaAn (Table 5.1), as expected for protons interacting with the anthranilate ion (An^-). The upfield shifts are significant for carbon atoms near the trimethylamine

Table 5.1 : ^1H Chemical Shifts (δ) of an Aqueous Solution of 10 mM CTAB with various concentrations of sodium anthranilate at 27 °C.

[NaAn]	Chemical Shifts (δ in ppm)					
(mM)	1	2	3+4	5	6	7
0	0.84	1.25	1.31	1.73	3.35	3.13
1	0.88	1.26	a	1.66	3.29	3.09
3	0.85	1.26	a	1.63	3.25	3.08
5	0.89	b	1.30	c	c	2.94
10	0.92	b	1.32	c	c	2.87

[a]signal merged into 2.

[b]signal merged into 3 and 4

[c]not resolved

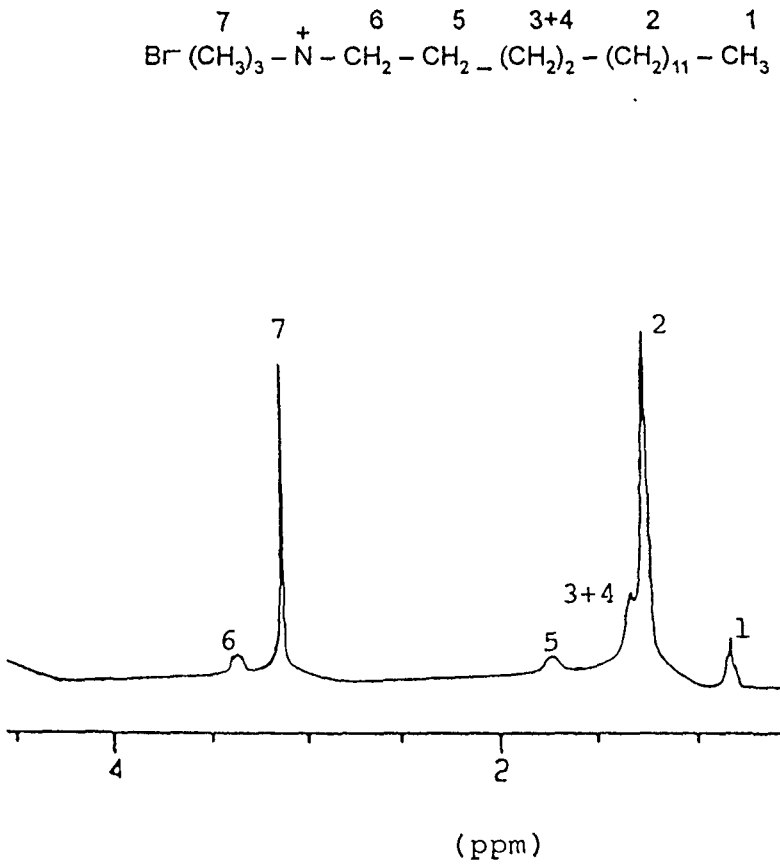


Fig. 5.1 : 300 MHz ^{1}H NMR spectrum of 10 mM CTAB in D_2O at 27 °C.

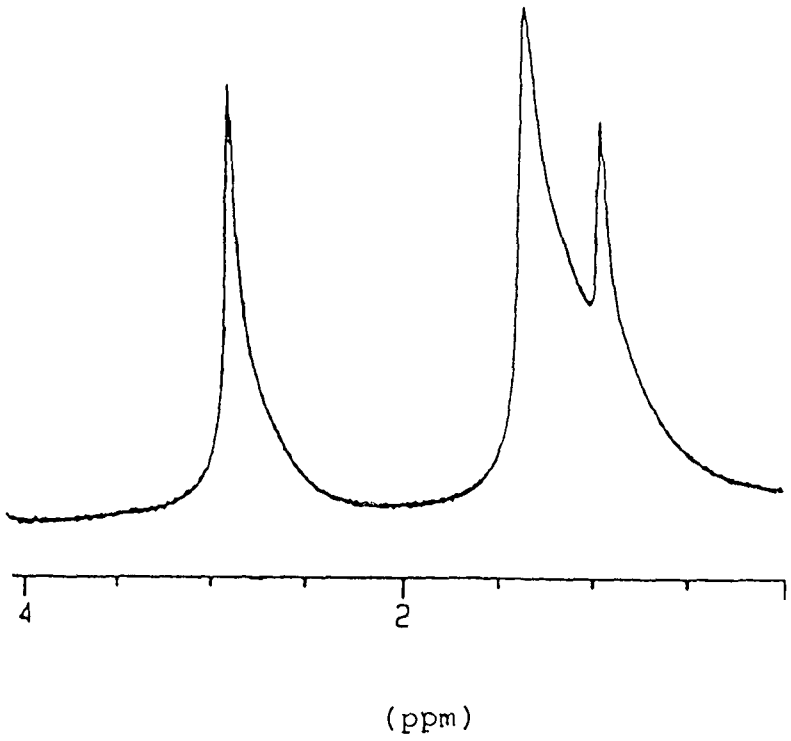


Fig. 5.2 : 300 MHz ^{1}H NMR spectrum of 10 mM CTAB containing 10 mM sodium anthranilate at 27 °C.

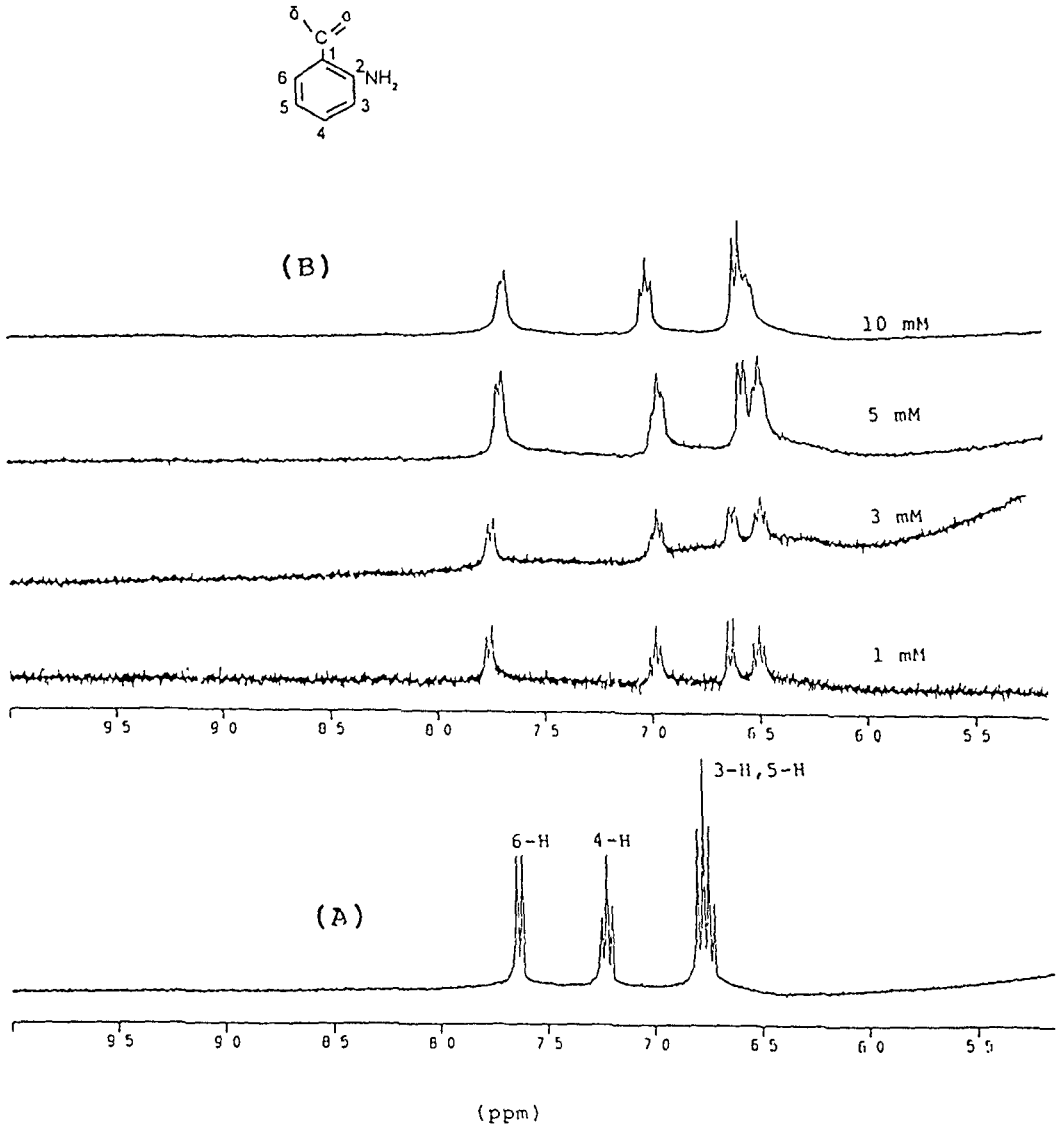


Fig. 5.3 : 300 MHz ^{1}H NMR spectrum of sodium anthranilate : (A) 10 mM pure NaAn; (B) with 10 mM CTAB at different [NaAn].

headgroup, whereas they are consistently unaltered toward the core carbon atoms of the CTAB monomer in the micelle. The large upfield shift of the first few carbon atoms (of the CTAB monomer) from the micellar surface may be due to partial replacement of water at the micellar surface by the anthranilate ion. When the molar ratio of salt to surfactant is close to unity, signals become very broad, making evaluation difficult, as shown in Fig. 5.2.

The above data (Fig. 5.2) suggest that adsorption of An^- on the micellar surface takes place by replacing water molecules from that region. The disappearance of peaks together with peak broadening is indicative of the presence of grown micelles in the system, which have features identical to those of the long polymeric micelles reported earlier.[354] SANS data on sodium salicylate – CTAB system also reveal similar micellar growth.[230]

Fig. 5.3 shows the ^1H NMR spectrum of the ring protons of the 10 mM NaAn solution in D_2O. The spectrum is first order and consists of three multiplets. The amino protons are not seen separately as they are labile, thus merging with the solvent peak. The spectra of ring protons at different concentrations of NaAn in 10mM CTAB are also shown in Fig. 5.3. From Fig. 5.3 the following points emerge: (a) 6-H proton remains (for all cases) in a polar environment, (b) 4-H proton is shifted to high field, implying that in the presence of CTAB micelles the *para* proton is shifted to a more nonpolar environment, and (c) 3- and 5-protons are affected differently and give a separate doublet and triplet at a higher field. The latter observation shows that even 3- and 5-protons behave differently despite their shift to a more nonpolar environment (owing to intercalation of An^- between CTAB monomers). The different shift for the

3-proton may be due to its proximity to the $-NH_2$ group. At a higher NaAn concentration (10 mM), the merger of the doublet and triplet (owing to the 3- and 5-protons, respectively) into a single quartet indicates a change in the effective environment (produced by grown micelles) experienced by these protons. This situation is similar to one in which no CTAB is present in the system (see Fig. 5.3A). This means that at higher NaAn concentrations, most of the An^- are not intercalated but adsorbed at the micellar surface and that they behave as if they are in an aqueous environment. These results suggest that initially An^- gets intercalated between the monomers owing to electrostatic and hydrophobic interactions followed by adsorption at the micelle – water interface. On the other hand, overall peak broadenings imply that mobility of the salt anion is restricted in the presence of micelles. This, of course, is expected as the two are oppositely charged.

Our NMR data allow us to conclude that two types of mechanisms are operating here: one is the intercalation of An^- between the head groups of the CTA^+ monomers, which gives a different effect from that due to the adsorption of An^- at the micellar surface; the above two phenomena are salt concentration dependent. Thus, other than orientation,[354] the nature of the group at the benzene ring and partitioning (intercalation/adsorption) of the additive near the micellar surface are also contributory factors of relevance for producing viscoelasticity in cationic surfactant solutions. These findings may be correlated with enzyme activity in a guest/host system, as lipase activities in long cylindrical micellar system are reduced than with shorter micellar aggregates.[357] The mobility of enzyme molecules was strongly reduced in grown micelles with the result that the enzyme did not have good access to the substrate and hence had a considerably hindered interaction.

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